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# Phosphorus in the Sediment of Agricultural Constructed Wetlands

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Department of Food and Environmental Sciences
Faculty of Agriculture and Forestry
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# PHOSPHORUS IN THE SEDIMENT OF AGRICULTURAL CONSTRUCTED WETLANDS

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Doctoral thesis in Environmental Soil Science

ACADEMIC DISSERTATION

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# Abstract

Phosphorus (P) losses from agricultural soils impair the quality of receiving surface waters by enhancing eutrophication. Most of the P carried by surface runoff and field drainage waters from clay soils in SW Finland is in particulate form, but more than half of the total P is potentially bioavailable. Thus, decreasing the load of suspended particles is important in controlling eutrophication.

Constructed wetlands and ponds (CWs) have become a popular means for trapping suspended material and particulate P in agricultural runoff. Efficient CWs can collect a large amount of particulate matter through sedimentation, and this needs to be removed regularly. Dredged sediment is often advised to be recycled back to the surrounding fields. However, the material ending up in CWs is subjected to several processes, which affect its P fractions and sorption-desorption characteristics. Changes in sediment characteristics occur 1) during erosion, 2) in the (anoxic) bottom of CW and 3) after dredging when the sediment is re-exposed to air.

This thesis examines P speciation and P sorption properties of sediments collected from five agricultural CWs established on clay soils, and compares the differences between the sediments and the source field soils in the catchments. Dredged, air-dried sediments were characterised separately from fresh sediments to assess the drying-induced changes in the P sorption-desorption properties. Phosphorus availability to Italian ryegrass (*Lolium multiflorum* L.) was tested by mixing CW sediment with soil in different ratios. Furthermore, the potential of using dredged sediment to immobilise soil P was assessed by exposing sediment-amended soil to simulated rainfall. Overall, the soils and sediments were analysed for several indices of P bioavailability and P sorption properties to predict the likely environmental consequences of applying CW sediments to fields.

The soils and CW sediments had similar total P contents, but clearly different P speciation when fresh sediments, air-dried sediments and the source soils were compared. In general, the sediment content of aluminium (Al)-associated P was significantly lower, and iron (Fe)-associated P significantly higher, than in the source soils. Reduced conditions, conducive to mobilisation of Fe-associated P and suggestive to Fe sulphide formation, were observed in all CWs. As a consequence of high clay and Al and Fe (hydr)oxide concentrations, possibly accentuated by Fe sulphide oxidation, dredged (re-oxidised) sediments showed a high affinity for P in sorption-desorption tests. In these tests a substantial decline in the equilibrium P concentration ($EPC_0$) was observed already at 2% to 5% (by fresh volume) sediment addition rates. The high affinity for P by sediment matter was also supported by observations in a growth experiment and simulated rainfall test. The lower the P plant availability for ryegrass and dissolved reactive P (DRP) concentration in percolating water, the more sediment was mixed into the soils.

The results suggest that the plant availability of P in CW sediments is very low due to the high concentrations of clay, and Al and Fe (hydr)oxides in sediments. Returning CW sediments to fields in large quantities is therefore likely to decrease the amount of P readily available for crop uptake. However, application of sediments dredged from CWs can be expected to immobilise soil P and decrease nonpoint source P loads when applied

to critical source area soils with environmentally problematic P saturation. A practical rate of sediment addition to the surface soil layer could be approximately 5% (by fresh volume).

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# Contents

# List of original publications and participation

This thesis is based on the following publications:

I Laakso, J., Uusitalo, R. & Yli-Halla, M. 2016. Phosphorus speciation in agricultural catchment soils and in fresh and dried sediments of five constructed wetlands. *Geoderma* 271, 18-26.

II Laakso, J., Uusitalo, R., Heikkinen, J. & Yli-Halla, M. 2017. Phosphorus in agricultural constructed wetland sediment is sparingly plant-available. *Journal of Plant Nutrition and Soil Science,* DOI: 10.1002/jpln.201700062

III Laakso, J., Uusitalo, R., Leppänen, J. & Yli-Halla, M. 2017. Sediment from agricultural constructed wetland immobilizes soil phosphorus. *Journal of Environmental Quality* 46, 356-363.

The publications are referred to in the text by their Roman numerals.

Johanna Laakso's (author) contribution:

I The first author was responsible for sampling and all experimental work. The author also had the main responsibility of writing the article in collaboration with the co-authors.

II Markku Yli-Halla and Janne Heikkinen constructed the original study setup idea. The preliminary pot experiment with chemical analyses was carried out by Janne Heikkinen. The first author performed the main pot experiment and laboratory analyses, and had main responsibility of writing the article in collaboration with the co-authors.

III The first author participated in planning the study and had main responsibility for the simulated rainfall study. Q/I plots and the Chang and Jackson P fractions were determined by Janette Leppänen. The first author had main responsibility of preparing the article in collaboration with the co-authors.

# 1 Introduction

The conflict between agriculture and the good ecological status of watercourses is a consequence of differing targets in the level of mineral nutrients in soil and water environments: high levels of easily available nutrients are preferred in agricultural fields to secure productivity, whereas modest concentrations are desired in watercourses to uphold reasonably low productivity. Hydrological systems in nature are open, and discharge from catchments end up in watercourses, which leads to carrying substances from a higher concentration (soil solution) to a lower concentration (surface runoff - ditch water - stream, lake, coastal waters).

Such diffuse nitrogen (N) and phosphorus (P) loading enhance eutrophication, impairing water quality, causing algal blooms and oxygen depletion, thus changing aquatic ecosystems. In the Baltic Sea, severe eutrophication manifests as the recent expansion of a large hypoxic (i.e. reduced sediment oxygen conditions) area less than 10 000 $km^2$ before 1950 to >60 000 $km^2$ since 2000. This is mainly caused by enhanced nutrient inputs from anthropogenic sources (Carstensen et al., 2014). As an example, agricultural P losses in Finland account for ~60% of all P entering surface waters (Valpasvuo-Jaatinen et al., 1997; Tattari et al., 2017).

P is needed as a macronutrient in agriculture to meet the demands of intensive crop production. A large input of fertilisers, among other technologies of the 'Green Revolution', has doubled global cereal production in the past 40 years (Tilman et al., 2001). Global food demand is projected to double in the next 50 years, which poses ever-growing challenges for food production in terrestrial and aquatic ecosystems (FAO, 2009; Rockström et al., 2009). Increasing food demand will not be met without fertilisers and sustainable practices in agriculture. Today, commercial fertilisers are responsible for at least 40 to 60% of the world's food production (Stewart et al., 2005).

The main source for phosphate fertiliser is phosphate rock, i.e., rocks containing high amounts of phosphate minerals. They are currently mostly mined from sedimentary deposits, the largest producer being Morocco with its 75% share of the world's known total phosphate rock reserves. Other significant deposits are found in China, the Middle East, northern Africa and the United States. Russia has large igneous phosphate resources in the Kola Peninsula. Estimates of the remaining availability of commercially recoverable P resources vary from 60–130 years (Steen, 1998) to 300–400 years (IFDC, 2010). Finland has rather small igneous phosphate rock deposits in Siilinjärvi and Sokli, which are unique phosphate resources because of the negligible contents of cadmium and uranium. The Siilinjärvi mine began operating in 1969, and it is the only phosphate mine in the European Union (EU). Annual phosphate fertiliser production is 500 000 tonnes, mainly used for domestic purposes, and with the Finnish diet our bodies can contain over 0.5 kg (1% of body mass) of Siilinjärvi phosphate!

Nearly all of the P used in Europe is imported, as is 76% of the P used by the agricultural sector (van Dijk et al., 2016). Half of the total P import is accumulated in

agricultural soils (net accumulation 4.9 kg $ha^{-1}$ $year^{-1}$ in EU-27) and half is lost through diverse waste flows (van Dijk et al., 2016). Many Western European countries have large accumulated reserves in their agricultural soils because of surplus application in the past. Despite this most EU countries still had positive annual agricultural balances in 2005 (van Dijk et al., 2016).

Phosphorus is recycled to a relatively small extent, with the exception of manure in animal production, which is almost fully recycled. Many waste flows in different sectors contain high P concentrations, which can be potential reserves for the future. The highest recycling potential is in wastewater sludge and biodegradable solid wastes in the food production chain (van Dijk et al., 2016). Phosphorus concentration, chemical quality (e.g. heavy metals), spatial location and technological costs are important aspects affecting P recyclability (Oenema et al., 2013).

Finland has been combatting eutrophication since the 1980s. Phosphorus removal from industrial and municipal wastewaters began in the mid-1970s, but effective means for decreasing diffuse loading are still being sought today. International and national commitments, including EU's Nitrates Directive (91/676/EEC) and the Water Framework Directive (2000/60/EG), along with the Helsinki Commission's (HELCOM's) Baltic Sea Action Plan (BSAP), are important in setting limits to nutrient losses from agriculture. National programmes (e.g. the Finnish Agri-environmental Programme) and EU-driven Finland's Rural Development Strategy (for 2014–2020) provide financial support for farmers and other groups in rural areas to develop the Finnish countryside into a better place for living, and reducing the P load to waters is explicitly stated as an important goal of these instruments. However, after decades of work, improvement in the water quality of agriculturally affected waters is barely visible (Tattari et al., 2017). Lakes situated in watersheds receiving waters from agricultural areas constitute the most eutrophic lake type in Finland (Ekholm and Mitikka, 2006). Nonetheless, substantial improvements towards more sustainable practices have occurred, as measured by fertiliser use, nutrient balances and improved agricultural practices (Aakkula et al., 2012). Mainly due to the decrease in mineral fertiliser use in Finland, the P balance of agricultural fields has decreased from +35 kg $ha^{-1}$ in the 1980s to +4 kg $ha^{-1}$ today (Official Statistics of Finland, 2016).

## 1.1 Phosphorus in soils and sediments

*Phosphorus in soils*

Apatite is a primary P mineral in most young soils, and is slowly weathered and transformed into secondary P minerals and organic P forms during soil development (Walker and Syers, 1976). Secondary P minerals in non-calcareous soils are associated with aluminium (Al) or iron (Fe) (Kaila, 1963), whereas secondary calcium (Ca) phosphates dominate in calcareous soils (Smeck, 1985). The P content of a typical soil profile is relatively high in the surface horizons (Ap in agricultural soils) and decreases to a profile minimum in the B horizon (Kaila, 1963; Peltovuori, 2006). In agricultural soils, fertiliser and manure applications, when associated with long-term positive P balances,

increase the P content in the Ap horizon. The P surplus is mainly recovered in the fractions of Al- and Fe-bound and organic P (e.g. Peltovuori, 2006). Negligible amounts of readily soluble P are found in subsoil horizons, indicating plant uptake from the B horizon and that P does not move from the Ap horizon to B horizons (Peltovuori, 2007). Fig. 1 shows inorganic P fractions and portions found in certain topsoils of cultivated land. The differences in P fractions between Finnish soils and other European soils may be due to fertilisation and farming practices, but also to soil properties, as Finnish soils are younger than soils in Central Europe. The less-ordered crystalline forms of Al and Fe (hydr)oxides in Finnish soils contribute to a higher P sorption capacity as suggested by the accumulation of Al-P and Fe-P (Fig. 1).

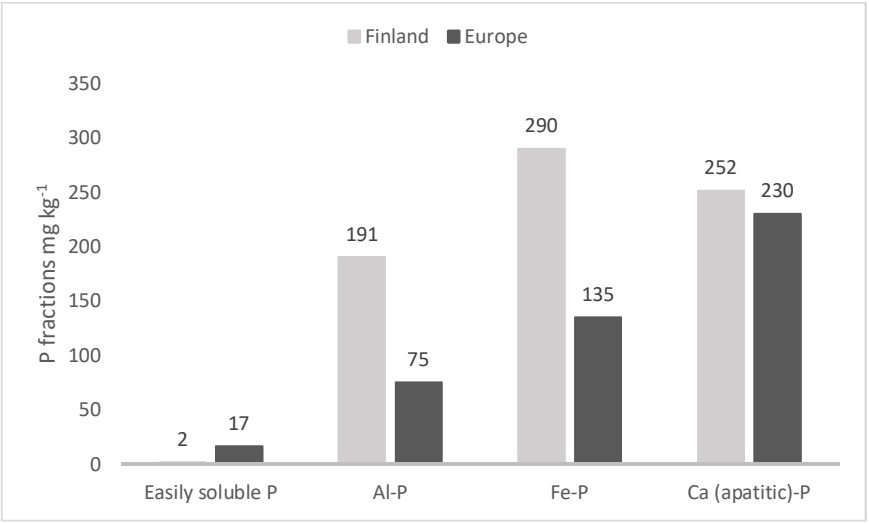



Figure 1. Inorganic P fractions (easily soluble P, Al-bound P (Al-P), Fe-bound P (Fe-P) and Ca-bound (apatitic) P) found in certain agricultural soils of Finland and Europe. Phosphorus fractions for Finnish soils (n=10) are calculated from Uusitalo and Tuhkanen (2000) and phosphorus fractions for European soils from Hartikainen et al. (2010) (n=19, calcareous soils and two Finnish soils were excluded from their original material. Countries included were UK, Italy, Austria and Hungary).

Most easily soluble P added to soil as fertiliser or manure is rapidly adsorbed by soil particles. Phosphorus is bound to short-range-ordered (hydr)oxides of Al and Fe, to the edges of clay minerals, and in Al and Fe complexes of organic matter (Walker and Syers, 1976). Most importantly, a specific ligand-exchange reaction happens on the (hydr)oxide surfaces, in which –OH or $–OH_2$ coordinated with a metal cation in the solid phase is replaced by phosphate ion ($H_2PO_4^-$, $HPO_4^{2-}$). The maximum number of phosphate ions that may be retained is limited by the number of sorption sites responsible for maintaining an equilibrium between soil pore water P and solid phase P in fertilised soils (Barrow, 1983). The number of P sorption sites (Al and Fe (hydr)oxides) already occupied by P is described by the degree of P saturation (DPS) concept, and indicates the potential desorbability of soil P. The increased saturation of Al and Fe (hydr)oxides due to former

farming practices of applying P in surplus have resulted in increased plant availability of P in the surface soils, but also increased P loss via leaching (Daniel et al., 1998).

A recently published large survey of the 35-year trend (1974–2009) in soluble nutrients (of pH 4.65 ammonium acetate-extractable P) in cultivated Finnish soils generally showed increasing concentrations of agronomic soil test P (Keskinen et al., 2016). During the 35-yr period, soluble P increased by 70% to 140% in clay soils and fine mineral soils, whereas a decreasing mean P was only visible in coarse mineral soils, despite fertiliser P sales currently being far lower than at the beginning of the study period in 1974 (Keskinen et al., 2016). Ylivainio et al. (2015), in turn, reported that 69% of cultivated clay soils in Finland have such high soil test P that annual P fertilisation is unlikely to provide any yield response. It thus appears that P fertilisation of fine-textured soils, which still show an increasing trend in soluble P, could be further reduced without compromising crop production potential (Valkama et al., 2011).

*Phosphorus in sediments*

Soils are parent materials for suspended particulate matter that ends up in recipient freshwater systems. In agricultural catchments, sediments found in adjacent watercourses are comprised of soil material eroded mainly from topsoils of cultivated land, transported by surface and subsurface runoff and finally settled to the bottom of receiving waters. Phosphorus amounts and fractions in the sediment are largely determined by their parent material along with the biogeochemical environment during runoff, settling and during residence in the bottom sediments (Hoffman et al., 2009; Kleinman et al., 2011; Kröger et al., 2013).

The vertical distribution of P in lake sediments often shows a decreasing concentration with sediment depth (Hartikainen 1979; Holtan et al., 1988). A high P concentration in surface sediment is due to recently settled material (loading) and possibly due to a delay in mineralisation because of an increased sedimentation rate and reduced biological activity introduced by low oxygen supply (Holtan et al., 1988). Of the inorganic P fractions, Al-P is highly affected by pH and Fe-P by redox conditions. Apatitic-P (Ca-P) is considered rather inert in sediments. The dissolved P from indices of Al and Fe oxides, along with the metal ions itself, tend to diffuse along concentration gradients from deeper sediment layers to the sediment surface and the sediment-water interface, where higher redox potential (Eh) and presence of soluble P favour its binding to metal phosphates (Holtan et al., 1988).

Phosphorus cycling in aquatic systems is related to carbon (C), Fe and sulphate ($SO_4$), as microbial degradation of organic matter in anaerobic sediments, such as in CWs, is coupled to Fe oxides and $SO_4$ as common electron acceptors. Fe oxides are reduced by two mechanisms; *via* microbial dissimilatory Fe reduction, where microbes use the oxides as electron acceptors in respiration, and *via* chemical reduction by sulphides ($H_2S$, $HS^-$) formed in microbial $SO_4$ reduction (Reddy and DeLaune, 2008). Microbial and chemical reductions of Fe have crucially different consequences for Fe cycling.

When Fe oxides are directly reduced by microbial dissimilatory reactions, the highly soluble Fe(II) produced is able to diffuse upward in the sediment pore water, and will be oxidised when encountering the oxygenated zone. Newly precipitated Fe oxides will be formed as a result, and these are capable of capturing high amounts of dissolved P. When organic C availability increases due to loading-induced primary production (eutrophication), Fe reduction gives way to $SO_4$ reduction. The end product, solid Fe sulfides (FeS, $FeS_2$), is permanently buried under anoxic conditions, and the ability of sediments to retain P is drastically reduced (Roden and Edmonds, 1997; Lehtoranta et al., 2009).

## 1.2 Phosphorus transport in runoff water

Phosphorus forms associated with P losses by runoff water are usually operationally defined as either dissolved or particulate P by filtering a water sample. Dissolved P can be divided into reactive (DRP) and unreactive P (DUP), depending on its reactivity with reduced molybdate reagent. DRP is readily available for biological utilisation e.g. for algae (Ekholm, 1994) and its role in the eutrophication of receiving waters has been emphasised (Baker et al., 2014). Dissolved unreactive P is thought to primarily contain organic P compounds and soil colloids that are able to pass through the pores (often 0.45 µm) of the used filter. Particulate P (PP) is defined as P bound to suspended mineral particles and organic matter in runoff water. Up to 50% of cultivated soils in Finland are silt and clay soils, drained by subsurface pipes and located in flat landscapes (Puustinen et al., 1994). Erosion via a subsurface drainage system in such soils is often attributable to preferential water flow through the soil profile (Øygarden et al., 1997; Uusitalo et al., 2001). Most of the P carried by surface runoff and subsurface drainflow from clay soils is in particulate form, the PP share being 63% and 73–94% of total P (TP) in studies performed in Sweden (Ulén and Persson, 1999) and Finland (Uusitalo et al., 2003), respectively. Particulate P can account for a remarkable reserve (up to 69%) of desorbable P (i.e. bioavailable P) in runoff from clay soils (Uusitalo et al., 2000), as P is desorbed from the suspended soil material trying to maintain the new equilibrium concentration. Thus, decreasing the load of suspended particles and preventing them from reaching the watercourses is also important from the eutrophication viewpoint.

Despite erosion control being seen as a means of P mitigation, Ekholm and Lehtoranta (2012) reviewed erosion processes from another viewpoint: could soil erosion counteract eutrophication by providing settling Fe oxides promoting counterparts (Fe) that retain P? High amounts of Fe oxides may inhibit $SO_4$ reduction, which otherwise would be reduced to sulphides and form insoluble, solid Fe sulphides unable to capture P (see 1.1 *Phosphorus in sediments*). They suggested that Fe oxides transported by eroded soil are needed in $SO_4$-rich systems to maintain the ability of sediment to retain P (Ekholm and Lehtoranta, 2012).

Quick and episodic P transport events can substantially contribute to annual P transport within catchments. The majority of annual P losses can occur from a small portion of a land area (i.e. critical source area) and only during a few severe storm events

(Sharpley et al., 1999), or during winter rains and spring snowmelt (Turtola et al., 2007) in Finland. As much as 76% of the annual TP was discharged during an 18-day period in December and January in the large catchment of Sagån (857 $km^2$), Sweden, with 36% cultivated land, average clay content of 42% and an annual average P loss of 0.4 kg $ha^{-1}$ (Ekstrand et al., 2010). This 0.4 kg $ha^{-1}$ P loss is equal to that measured for 11 Swedish fields in a 21-year monitoring study (Ulén et al., 2000). Long-term (1981–2010) monitoring of P loss from agricultural land in Finland suggests that mean annual P loss figures would be substantially higher, averaging 1.1 kg P $ha^{-1}$ $year^{-1}$ (Tattari et al., 2017). Since P loading is event-driven (including heavy rains), mitigation measures to reduce P should be able to capture P that is lost during these types of events. A further challenge may be brought about by projected climate change, with increased rainfall in winter, but lower spring flow peaks because of higher winter temperatures (Arnell, 1999). Erosion rates are expected to increase due to increased winter rains, especially if soils are left without plant cover over winter.

Phosphorus losses from agricultural soils can be controlled either at the sources or during transport. Reducing nutrient input has been suggested as the most cost-effective way to cut down the load in the Baltic Sea region (Granstedt, 2000). This means that fertilisation should be reduced to equal the P levels removed by the following crop, and further adjusted according to the current soil P status. Liming or reduced tillage are suggested for improving soil structure and aggregate stability, as they can increase P uptake by plants and concurrently prevent soil loss by erosive water forces (Tebrügge and Düring, 1999). Finally, to capture eroded soil and P, efforts have been made to prevent eroded materials from entering watercourses by establishing buffer zones, sedimentation ponds and wetlands.

## 1.3 Constructed wetlands – a popular attempt to restrain eutrophication

Constructed wetlands (CWs) can function as buffers for nutrient retention between catchment and receiving watercourses. In this viewpoint, wetlands form a critical boundary between catchments and adjacent streams, lakes and coastal waters, as all of these ecosystems are hydrologically connected.

Constructed wetlands are built for several purposes such as water treatment (Fisher and Acreman, 2004), water storage (Barnett et al., 2000), as wildlife habitats (Knight, 1997) and to increase biodiversity (Hansson et al., 2005). In this thesis CWs are viewed as a means of water protection. Constructed wetlands collect waters *via* inlet ditches, where surface runoff and subsurface drainage waters are conducted from the catchment area. Nutrient removal in CWs is achieved through a combination of sedimentation, filtration, chemical sorption and precipitation, microbial interactions and by vegetal uptake (Reddy and DeLaune, 2008; p. 328). However, the retention of soil particles by sedimentation is a key factor in fine-textured areas (Johnston et al., 1990; Johannesson et al., 2015), as P is mainly bound to clay particles. In Finland, CWs have become popular

tools in attempts to decrease nutrient and eroded soil loading from agricultural land to watercourses. Since Finland joined the EU in 1995, CWs became part of the agro-environmental support scheme and more than a thousand subsidised CWs have been established (Westinen, personal communication, 2015).

Perhaps the most challenging aspect in the design of CWs that treat agricultural runoff is how to cope with the high variability in seasonal hydraulic load. In general, the ability of a wetland to retain nutrients increases with the water retention time. This is affected by water discharge and design factors such as wetland surface area, depth and other hydraulic properties. For a satisfactory relative particle retention, Koskiaho (2006) suggested a 2% ratio (CW area in relation to catchment area) as a "rule of thumb". However, Kynkäänniemi (2014) emphasised site-specific factors over size, as particle retention may differ among wetlands of similar size. In practice, landowners prefer smaller CWs to save productive land and construction costs. To qualify for subsidies from the European Agricultural Fund for Rural Development (EAFRD) in Finland, a CW must be larger than 0.3 ha, it must comprise more than 0.5% of the upstream catchment area and more than 10% (before 2014 the requirement was 20%) of the catchment area must consist of agricultural land.

Nutrient removal in CWs treating wastewaters has been extensively studied (Hammer, 1989; Kadlec and Knight, 1996). Much less is known about the retention processes of wetlands that receive unregulated inflows i.e. diffuse loading from agricultural land. CWs have been suggested to effectively remove P despite the large variation of P concentrations in inflow waters (Mitsch et al., 1995), but the physicochemical characteristics of various wetland sediments are important, as they influence the inorganic P sorption dynamics (Ryden and Syers, 1975) and the behaviour of organic P. Few studies have been published concerning P dynamics in sediments of agricultural CWs. Reddy et al. (1995) characterised CW sediments for P fractions and found that inorganic P was mostly associated with Fe and Al (hydr)oxides (43% of TP), and that P sorption capacity highly correlated with oxalate-extractable Fe and Al, and total organic C content. In a newly constructed CW in Sweden, P fractions were similarly mainly Fe- and Al-bound (39% of TP) and organic (38% of TP) (Johannesson et al., 2011). Dunne et al. (2005) studied the P sorption properties of two agricultural CW sediments in Ireland, and found a high ability to retain P (618–1464 mg P $kg^{-1}$ retention in sediment matter) from overlying water in oxic conditions.

A number of research papers have been published concerning nutrient and particle retention capacity of agricultural CWs in Finland (Uusi-Kämppä et al., 2000; Koskiaho et al., 2003; Liikanen et al., 2004; Valkama et al., 2017), also with chemically assisted phosphorus precipitation (Uusitalo et al., 2013). In general, agricultural CWs show high P retention, the removal efficiency being dependent on retention time, which is highly affected by the relative area of CW (of its catchment). Koskiaho (2006) studied CW hydrology and hydraulics, and describes in detail how CWs should be designed and dimensioned to optimise their performance. Numerous studies conducted in northern Finland report the water purification ability of wetlands receiving waters from peat mining

areas (e.g. Heikkinen and Ihme, 1995; Heikkinen et al., 1995; Ronkanen and Kløve, 2009; Heiderscheidt et al., 2013). Urban wetlands designed for improving water quality and as wildlife habitats have also been studied (Wahlroos et al., 2015), but such studies are rare.

Plenty of soil material (up to 22–90 kg $m^{-2}$ $year^{-1}$) originating from surrounding fields may accumulate in CWs over time (Braskerud et al., 2000; Johannesson et al., 2011). This has to be removed regularly to sustain efficient particle retention and to prevent accumulated sediment from escaping downstream. The Ministry of Agriculture and Forestry in Finland recommends sediment dredged from CWs to be recycled back to fields, with the aim of closing the agricultural P cycle. However, the consequences on soil properties as a growth medium after sediment application have been rarely investigated. A few studies have been published concerning sediment reuse from various sources. Rahman et al. (2004) suggested the sediment of fishpond in Thailand to be suitable for crop production, as the sediment would increase soil organic matter content. Ockenden et al. (2014) considered that the application of dredged sediment could have value as a soil replacement method of eroded matter, but not as fertiliser in the UK. Quite opposite to two former examples, Zhang et al. (2002) stated that lake sediments retain P strongly when applied to sandy soils in Florida. However, no studies appear to directly address the effects on P plant availability or P sorption characteristics in using agricultural CW sediment as recycled material in fields. Here is the starting point of this thesis.

# 2 Aim, objectives and hypotheses

The aim of this thesis was to gain better understanding of the changes in P solubility and P sorption properties of clayey soil material when transported from the catchment field, sedimented in a CW and returned to fields after dredging. The practical aim was to assess the likely agricultural and environmental consequences of the field application of CW sediments.

Specific objectives for each paper included in this thesis were:

I To investigate how the transport of soil material from the field into CW influences its P speciation. The starting hypothesis was that plant-available P is released from eroded soil in runoff water during the erosional transport. Once sedimented in CW, the material likely becomes periodically depleted in oxygen, and re-oxidised when dredged. The second objective was to test how re-oxidation of the sediment matter after dredging affects the P pools and the P sorption capacity of the material. The hypothesis was that due to high clay, and Al and Fe (hydr)oxide contents, along with the oxidation of reduced material, the sediment is low in readily soluble P and has a high ability to retain P.

II To examine P sorption-desorption characteristics and directly determine P availability to Italian ryegrass (*Lolium multiflorum* L.) when CW sediment is mixed with soil in various ratios. The hypothesis was that the addition of CW sediment to soil, by increasing P retention, decreases P solubility in the soil. It was also hypothesised that CW sediment is depleted in plant-available P and thus has a limited value as a P source to plants.

III To investigate whether increasing quantities of dredged CW sediment mixed with topsoil increases P retention in soils and decreases P concentrations in runoff water. The starting hypothesis was that sediment additions increase P retention in soil by chemical adsorption, as metal (hydr)oxides that have plenty of free sites for P retention are introduced to the soil. The high P retention of the sediment could thus be utilised in P mitigation in critical source areas of P loading.

# 3 Materials and methods

## 3.1 Study sites

The study sites represented five agricultural CWs established on fine-textured mineral soils in SW Finland (Table 1, Fig. 2 and 3). In all surrounding catchments the soil type was Vertic Stagnosol according to the WRB system (IUSS Working Group WRB, 2014). The CWs had been constructed 6–17 years before the start of the study in 2012. Two of the sites (Kakskerta and Nautela) had chemically assisted P precipitation, with aluminium chloride solution (trade name Kempac 18, Kemira Kemwater, Helsinki, Finland) at Kakskerta and granular ferric sulphate ($Fe_2(SO_4)_3$, trade name Ferix-3, Kemira Kemwater, Helsinki Finland) at Nautela added into the water entering the CWs. These chemical treatments had been performed for nine years at Kakskerta (since 2003), with the exception of occasional interruptions, and for 1.5 years at Nautela (since 2011; for a more detailed description of the Nautela site, see Uusitalo et al., 2013). Arable land comprised 50–100% of the land use in the five catchments (Table 1). The areas were mostly used for growing cereals. The fields had subsurface pipe drainage systems at all sites. The catchment areas around the CWs at Liedonperä, Hovi and Nautela had conventional crop rotation with autumn ploughing, whereas the catchment at Kakskerta was agricultural grassland, and a no-till cropping system was applied at Ojainen. Only Hovi and Liedonperä CWs met the mandatory subsidy requirements on the size and share of the catchment area (i.e. 0.5% of the catchment area). The Hovi CW was an order of magnitude larger (5%) than the recommended size in relation to the catchment. A more detailed description of Hovi CW can be found in Koskiaho et al. (2003) and Liikanen et al. (2004).

Table 1. Size and characteristics of the Ojainen, Liedonperä, Hovi, Kakskerta and Nautela constructed wetlands (CW) and their catchments.

| Site (Municipality) | Year established | Size $m^2$ | Catchment area, $km^2$ | CW as % of catchment area | Arable land in catchment % | Dominant soil texture in catchment[a] | Chemical, dosing, $kg:m^3$ water |
|---|---|---|---|---|---|---|---|
| Ojainen (Jokioinen) | 2000 | 370 | 0.16 | 0.23 | 100 | silty clay | - |
| Liedonperä (Tarvasjoki) | 1995 | 4850 | 0.99 | 0.49 | 50 | silty clay loam | - |
| Hovi (Vihti) | 1998 | 6000 | 0.12 | 5.0 | 100 | clay | - |
| Kakskerta (Turku) | 2006 | 850 | 0.73 | 0.12 | 64 | clay | aluminium chloride, 1:30 |
| Nautela (Lieto) | 2005 | <100 | 0.61 | < 0.02 | 63 | silty clay | ferric sulphate, 1:50 |

[a]According to USDA texture classes.

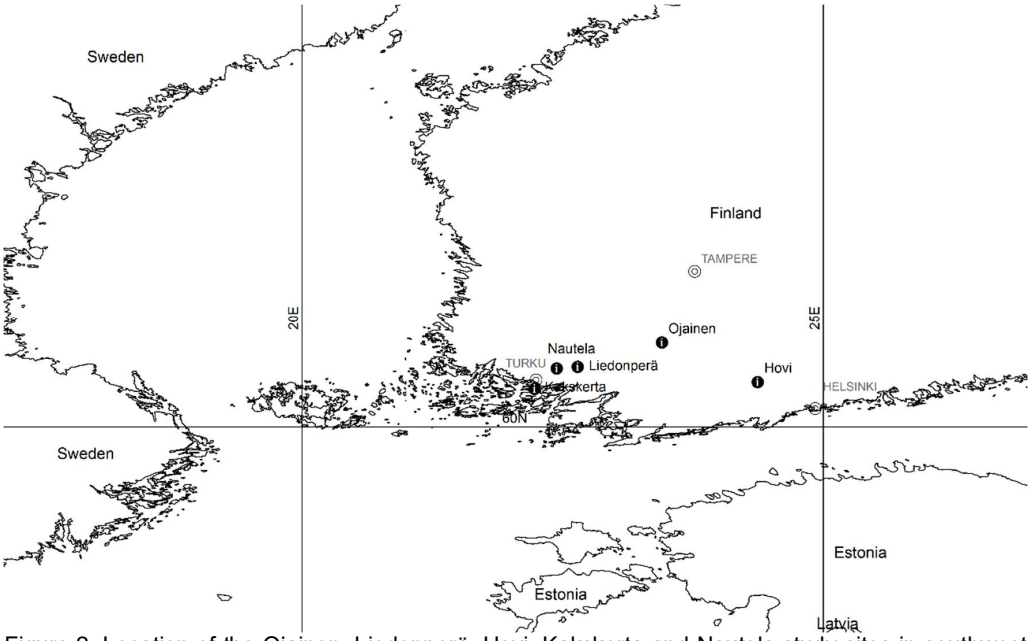


Figure 2. Location of the Ojainen, Liedonperä, Hovi, Kakskerta and Nautela study sites in southwest Finland.

Figure 3. Left to right: the Ojainen, Liedonperä and Nautela CWs. The ferric sulphate doser in the picture at Nautela. Photos: Johanna Laakso.

## 3.2 Soil and sediment samples

Soil samples for the studies were collected in August 2012, and additional samples for later experiments complemented with sampling were collected August 2013. Composite soil samples were taken from the surrounding fields of each CW on three transects with slopes that visually represented the field area from which most of the CW sediments would likely originate. The samples representing each transect consisted of three subsamples taken approximately every 30 m from the CW, and diagonally to the main slope. In addition, a soil sample with excessive soil test P (STP, 210 mg ammonium acetate-extractable P ($P_{Ac}$) $l^{-1}$) was collected from a garden plot in Rehtijärvi, Jokioinen for the rainfall simulation study (Paper III). Sampling was carried out with a spade from the Ap horizon (0–20 cm depth). Subsamples of the soils were allowed to air-dry, were crushed in a mortar and sieved (2 mm) for later analyses. The remaining samples were stored in sampling moisture at +5°C in darkness.

Sediment sampling was conducted with a Limnos (Limnos Ltd., Turku, Finland) sediment sampler (acrylic plastic cylinder, 94 mm in diameter, 600 mm in length). Samples were taken from open-water areas, when present, in the deepest parts of the CWs, with a water depth of ca. 1–2 m, in August 2012 and August 2013. The depths of the relatively loosely settled sediment profiles reached with the sampler were approximately 30 cm at Ojainen, Liedonperä and Hovi. However, because the Kakskerta and Nautela CWs were built by widening a ditch, there were no deeper open-water areas and the sediments were collected with a long-handled dipper at approximately 0–10 cm depth.

Redox potential and pH of the sediments from 0–10 cm depth were measured immediately in the field with a platinum electrode and pH electrode using a handheld Scientific Instruments IQ170 pH/Eh meter. The samples were then stored in plastic buckets fitted with lids and transported to the laboratory within two hours. A subsample of each sediment was allowed to air-dry, crushed in a mortar and sieved (2 mm) for later analyses. For incubations, wet sediment was sieved (4 mm) to remove plant residues and larger debris before it was mixed with the soils. The remaining samples were wet-stored at +5 °C in darkness until analysed.

## 3.3 Methods and experimental designs

The design of the experiments and the major analyses for P content and sorption/desorption properties in different circumstances are described in Table 2. Details of supporting analyses can be found in the original publications. Paper I mainly involves the characterisation of P pools in soils and sediments. Paper II presents the results of a pot experiment where plant availability of P in the sediments was studied. Paper III involves a rainfall simulation study for soil with increasing sediment additions. Table 2 compiles the experiments and procedures, samples and number of replicates used.

Table 2. Summary of the main experiments and procedures, the constructed wetland (CW) sites, samples and number of replicates conducted in the original papers.

| | Study subject | Experiment description (Reference) | CW site | Sample type | Number of replicates |
|---|---|---|---|---|---|
| Paper I | P content and P sorption properties | Anion exchange resin extraction (potentially desorbable P) (Sibbesen, 1977, 1978) | All | Soil, fresh and air-dried sediment | 3 |
| | | Bicarbonate-dithionite extraction (redox-sensitive P) (Uusitalo and Turtola 2003) | | Fresh and air-dried sediment | 4 |
| | | Total P (Bowman, 1988)<br>Organic P (Olsen and Sommers, 1982) | | Soil, air-dried sediment | 2, 3 |
| | | Inorganic P fractions (Chang and Jackson (1957) modified by Hartikainen, 1979) | | Soil, fresh and air-dried sediment | 3 |
| | | Oxalate extractable Al and Fe (Schwertmann, 1964)<br>Degree of P saturation (Lookman et al., 1995; Peltovuori et al., 2002; Hartikainen et al., 2010) | | Soil, fresh and air-dried sediment | 2 |
| Paper II | Availability of sediment P to plants | Simple sorption test for incubated soil-sediment mixtures | Ojainen soil and sediment, Liedonperä soil and sediment | Soil, fresh sediment | 3 |
| | | Pot experiment for ryegrass in a greenhouse | | Soil, fresh sediment, plant material | 3 |
| Paper III | P sorption by sediment | Q/I experiment for incubated soil-sediment mixtures (Hartikainen, 1991) | Ojainen and Rehtijärvi soil, Liedonperä sediment | Soil, fresh sediment | 3 |
| | | Simulated rainfall for incubated soil-sediment mixtures, percolating water analyses | | Soil, fresh sediment | 3 |

### 3.3.1 Analytical basis for studying sediment properties

The sediment samples were analysed for several indices of P, especially in relation to P bioavailability, P sorption properties and to evaluate the risk of P loading to watercourses. These analyses included chemical fractionation, anion exchange resin (AER) extraction, which is a measure of potentially desorbable P under oxic conditions, bicarbonate-dithionite (BD) extraction, which dissolves redox-sensitive P, and by means of a desorption-sorption isotherm technique (Q/I-plots). The P sorption components, i.e. short-range ordered (hydr)oxides of Al and Fe, were determined with ammonium oxalate extraction.

All analyses described above, except the Q/I-plots, were carried out both with fresh and air-dried sediment samples to illustrate the changes upon dredging and drying of the sediment. However, "fresh" sediment samples, which were assumed to be partly in reduced state, may have been exposed to oxygen during sampling and storage, because no $N_2$-shielding was used. As the principal purpose of this study was to investigate the recycling of dredged sediment material, sediment oxidation was considered non-critical for the aim of the work. In any case, at least parts of the sediment samples had remained in reduced state, because a few months later black sulphide spots were visible in the stored samples. When analysing "fresh" samples, oxidation likely also occurred during the actual analysis, for example during the extraction. Therefore these measurements rather represent a newly oxidised state of sediment samples.

### 3.3.2 Laboratory analyses

*Anion exchange resin (AER) extraction*

To estimate the amount of potentially desorbable P from soil and sediment material, soil samples and fresh and dried sediment samples were extracted four weeks after sampling using AER as a sink for P desorbed from soil (Sibbesen, 1977; Uusitalo and Ekholm, 2003). In this method, 1 g strong basic AER (Dowex 1 × 8, Fluka Chemika, Neu-Ulm, Germany), with ca. 2 mmol anion exchange capacity, was enclosed in small nylon netting (Sefar Nitex, Sefar Inc., Heiden, Switzerland) bags with mesh size 0.25 mm. Before extraction, AER was converted into $HCO_3^-$form by washing the bags for four h with two portions of 0.5 M $NaHCO_3$ solution (Sibbesen, 1978). The extraction was performed with a 1-g sample of dry matter and 40 ml deionised water in a 50-ml extraction tube with one AER bag. The tubes were shaken overnight (20 h) on an orbital shaker at 100 rpm. The AER bag was then removed, washed with deionised water and shaken in 40 ml 0.5 M NaCl for four h to displace P from the AER into the solution. The bag was removed from the extraction vessel and the NaCl solution was acidified with 1 ml 6 M HCl and allowed to stand overnight to remove carbon dioxide ($CO_2$). The P concentration of the NaCl solution was measured with a Lachat (Milwaukee, WI) QC Autoanalyser using the method of Murphy and Riley (1962).

*Extraction of redox-sensitive P*

Both fresh and dried sediment samples (but not soil samples) were extracted with bicarbonate-buffered sodium dithionite (BD) solution to analyse redox-sensitive P, as described by Uusitalo and Turtola (2003). In brief, 0.2 g sediment samples were weighed into 250-ml plastic bottles and 100 ml of deionised water was added. Aliquots of 2.5 ml of both solutions were added to the samples, bicarbonate (0.298M $NaHCO_3$) being prepared for daily use and the dithionite solution (0.574 M $Na_2S_2O_4$) just before extraction. The sample bottles were capped and shaken on an orbital shaker for 15 min at 120 rpm. After extraction, the samples were immediately filtered through a 0.2-µm Nuclepore polycarbonate filter (Whatman, Maidstone, UK). Then 10 ml of filtrate was digested with 4 ml persulphate (50 g $K_2S_2O_8$ in 1 l of 0.4 M $H_2SO_4$) in an autoclave (+120 °C, 100 kPa, 30 min) to oxidise the excess dithionite. The P concentration was measured as in the AER-P analysis.

*Total P and organic P*

Total P in the soil and dried sediment samples was determined with the $H_2SO_4$–$H_2O_2$–HF extraction method of Bowman (1988). Organic P was determined by the ignition method of Olsen and Sommers (1982) using 0.5 M $H_2SO_4$ extraction (1:50 w:v; 16 h). Phosphorus concentrations were determined using the method of Murphy and Riley (1962) with ascorbic acid as the reducing agent. The extracts were analysed with a Lachat (Milwaukee, WI) QC Autoanalyser and a spectrophotometer (Shimadzu UV-120-02, Kyoto, Japan) for total P and organic P measurements, respectively.

*Inorganic P fractions*

The inorganic P reserves in the soil and (fresh and dried) sediment samples were determined by the Chang and Jackson (1957) method as modified by Hartikainen (1979). Triplicate samples were sequentially extracted, using a soil-to-solution ratio 1:50, with: i) 1 M $NH_4Cl$ (30 min), assumed to extract the most easily soluble P and exchangeable Ca; ii) 0.5 M $NH_4F$ (pH 8.5) (1 h) for Al-bound P; iii) 0.1 M NaOH (16 h) for Fe-bound P; and iv) 0.25M $H_2SO_4$ (1 h) for Ca-bound apatitic P. The suspensions were centrifuged (15 min, 3846×*g*) and $NH_4Cl$ extracts were filtered through Munktell OOR paper filters (Munktell Filter AB, Grycksbo, Sweden). For $NH_4F$ and NaOH extracts, dissolved humus was removed by precipitation with 0.5 M $H_2SO_4$ (Hartikainen, 1979). The soil matter pellet remaining after the $NH_4F$ and NaOH extractions was washed with saturated NaCl solution to prevent carryover of P to the following steps. The P concentration was analysed with the molybdenum blue method of Murphy and Riley (1962) using a spectrophotometer (Shimadzu UV-120-02, Kyoto, Japan).

*Soil test P*

Determination of soil test P (STP, $P_{Ac}$) was based on extraction with acidic (pH 4.65) ammonium acetate according to the Finnish agronomic soil testing protocol (Vuorinen and Mäkitie, 1955). The extracting solution is 0.5 M in acetic acid and 0.5 M in

ammonium acetate concentration. Shaking is performed at a 1:10 soil/solution ratio, end-over-end, for one h, followed by colorimetric P analysis.

*Oxalate-extractable Al and Fe*

Short-range ordered (hydr)oxides of Al and Fe ($Al_{ox}$ and $Fe_{ox}$) were analysed in soil and (fresh and dry) sediment samples using the ammonium oxalate extraction method of Schwertmann (1964). Duplicate 0.5 g samples were extracted with 25 ml acidic (pH 3.0) ammonium oxalate solution (57% 0.2 M $(NH_4)_2C_2O_4 \times H_2O$, 43% 0.2 M $C_2H_2O_4 \times 2\ H_2O$) for four h in the dark. After centrifuging (15 min, 3846×*g*), the aliquots were filtered through a blue ribbon paper filter (<2 mm) (Schleicher & Schuell) followed by inductively coupled plasma determination.

*P sorption capacity and degree of P saturation*

The P sorption capacity (PSC) was calculated as (Lookman et al., 1995):

$$PSC = 0.5 \times (Al_{ox} + Fe_{ox}) \quad (1),$$

where PSC, $Al_{ox}$ and $Fe_{ox}$ are in mmol $kg^{-1}$. A coefficient of 0.5 is generally used to calculate PSC for non-calcareous soils in northwestern Europe (e.g. Schoumans, 2000). The degree of P saturation ($DPS_\Sigma$) was calculated according to Peltovuori et al. (2002) using the sum ($P_\Sigma$) of the Chang and Jackson (1957) P fractions $NH_4Cl$-P, $NH_4F$-P, and NaOH-P as:

$$DPS_\Sigma = 100 \times P_\Sigma/PSC \quad (2),$$

where $DPS_\Sigma$ is expressed in percent and $P_\Sigma$ and PSC are expressed in millimoles per kilogram. The DPS was also calculated separately for $Al_{ox}$ and $Fe_{ox}$ on a molar basis (Lookman et al., 1995; Hartikainen et al., 2010) as:

$$DPS_{Alox} = 100 \times Al\text{-}P/0.5 \times Al_{ox} \quad (3)$$

$$DPS_{Feox} = 100 \times Fe\text{-}P/0.5 \times Fe_{ox} \quad (4),$$

where Al-P is $NH_4F$-extractable P and Fe-P is NaOH-extractable P by Chang and Jackson (1957) fractionation.

### 3.3.3 Pot experiment supported by a simple P sorption test

The Ojainen and Liedonperä soils and the corresponding CW sediments were chosen for a pot experiment in which ryegrass was grown in soil-sediment mixtures. The study was conducted in a greenhouse in May–June 2013. A complementary P sorption test was also conducted to evaluate changes in P sorption properties without plants.

*Simple sorption test*

The Ojainen and Liedonperä soils were incubated with increasing amounts of their respective CW sediment (0% (control), 12.5%, 25%, 50% and 100% (volume) of sediment on a dry weight (d.w.) basis), with triplicate samples of all mixtures. The

mixtures (comprising in total 10 g dry matter) were set at 35% moisture content and kept at +21 °C for four weeks. The moisture content was checked and re-adjusted as necessary twice weekly, and the samples were stirred lightly.

After the four-week incubation, 1 g (dry matter) subsamples were extracted with deionised water ($P_w$) and with a standard P solution containing 2 mg P $l^{-1}$ at a soil-to-solution ratio of 1:60 (w:v) for 16 h. Following extraction, the suspensions were centrifuged and filtered through a 0.2-µm Nuclepore filter (Whatman, Maidstone, UK) and analysed for P according to Murphy and Riley (1962), with a Lachat (Milwaukee, WI) QC Autoanalyser. The amount of desorbed or adsorbed P (Q) was calculated as in Eq. (5) in a quantity/intensity experiment, but a linear equation was used to estimate x-axis intercept ($EPC_0$'):

$$Q = mI + b \quad (5),$$

where *m* is slope and *b* is y-axis intercept. For the estimate of equilibrium P concentration (here termed as $EPC_0$'), the x-axis intercept was calculated (Q=0). The values of *m* and *b* were determined by linear regression. This simple two-point P sorption test does not give accurate estimates of $EPC_0$ in its conventional meaning, or the slope at the x-axis intercept, but indicates the P affinity of the soil-sediment mixtures and hence the direction of $EPC_0$ change.

*Pot experiment*

*Preliminary test*

In a preliminary test of the sediment P availability to Italian ryegrass (*Lolium multiflorum* L.), field soil (Ap horizon) and sediment (0–10 cm) from the Liedonperä site were used as a growth medium (Heikkinen, 2011). The same site (for soil and sediment samples) was used also in the main growth experiment. In this experiment, 100 g soil or 100 g sediment mixed with 200 g quartz sand was used as the growing medium for two cuts of ryegrass. Phosphorus (as $KH_2PO_4$) was applied to both mixtures at a rate of 90 mg $kg^{-1}$. Other nutrients were supplied in amounts that would not restrict plant growth (see the main experiment below). For the second cut, a supplementary dose of 270 mg P $kg^{-1}$ (as $Ca(H_2PO_4)_2$), 100 mg N $kg^{-1}$ (as $NH_4NO_3$) and 50 mg potassium (K) $kg^{-1}$ (as KCl) was supplied.

*Main growth experiment*

For the main greenhouse experiment, the growth medium was composed of soil and sediment mixtures to investigate how increasing sediment addition affected plant P uptake. The two soils and corresponding CW sediments were sieved (4 mm) moist, the moisture content of all samples was determined and the growth medium was prepared on a dry weight basis. Sediment addition rates of 0% (control), 12.5%, 25% and 50% to soil were tested. The total mass of each mixture was 100 g dry matter and triplicate samples were prepared for each mixture. The mixtures were allowed to equilibrate at +21 °C in the laboratory for five days at a moisture content of 35% (adjusted with deionised water).

Because the high clay content of the sediment could have resulted in an overly dense growth medium at higher inclusion rates, causing adverse effects on aeration of the medium, 200 g of quartz sand (0.5–1.0 mm) rinsed with deionised water was applied to each mixture. Around two-thirds of each growth medium prepared was placed in a 500-ml pot and nutrient solutions were pipetted and mixed in. The remaining one-third of the medium was then added, Italian ryegrass (*Lolium multiflorum* L.) seeds (0.35 g $pot^{-1}$) were sown and 60 g of quartz sand was applied on the surface of each pot to reduce evaporation. The moisture content was set at 35% with deionised water. The pots were then transferred to a greenhouse (+20 °C, daylight 6:00–22:00), placed in randomised order on trays on a table, and covered with perforated plastic film until germination (for six days).

Two P fertilisation levels were tested: 0 and 45 mg $pot^{-1}$ (150 mg $kg^{-1}$ as $KH_2PO_4$ solution). To supply other nutrients, solutions containing the following elements were pipetted into the pots: 300 N mg $kg^{-1}$ (as $NH_4NO_3$), 200 mg K $kg^{-1}$ (as KCl), 66 mg sulphur (S) $kg^{-1}$ and 50 mg magnesium (Mg) $kg^{-1}$ (as $MgSO_4$). Growing plants were watered by hand with deionised water to the soil surface every two or three days. If leachate ran on the tray after watering, water was poured back to the soil surface. The moisture content of 35% was frequently checked by weighing some of the pots.

Three cuts of ryegrass were taken. After the first and second cuts, supplementary doses of N (300 mg $kg^{-1}$ as $NH_4NO_3$) and K (200 mg $kg^{-1}$ as KCl) were given in four different proportions to ensure a sufficient supply for the following cut, but P was applied only at the beginning of the experiment.

Micronutrients were not given. Based on experience of the authors in Paper III, zinc (Zn) deficiency, for example, is very rare in Finnish soils. Although pH of growth media was 6.7–7.3, it was expected to decrease during sediment oxidation in the soil–sediment mixtures heavily fertilised with nitrogen.

Plant shoots were harvested using scissors to cut 2 cm above the soil surface on three occasions: 30, 50 and 70 days after sowing. The shoots were placed in pre-weighed paper bags, dried at +60 °C for five days and weighed for dry matter yield. For nutrient analyses, the ryegrass shoots were ground in a hammer mill and ashed at 500 °C for three h. The residues were dissolved in 5 ml of 6 M HCl and evaporated to dryness on a sand bath. Cooled residues were flushed with hot 0.24 M HCl on funnels equipped with paper filters (white ribbon; Schleicher & Schuell, Dassel, Germany) and filtered into 50 ml volumetric flasks that were then filled to the mark with 0.24 M HCl. The filtrate was analysed for P using ICP-AES (Thermo Jarrel Ash, Franklin, MA, USA).

Utilisation of P by ryegrass was calculated according to Morel and Fardeau (1990) as the percentage of fertiliser P taken up by ryegrass in all three cuts. To obtain the final P utilisation value, P uptake by the P-unfertilised control was subtracted.

### 3.3.4 Rainfall simulation study and Q/I experiment

For the simulated rainfall and Q/I tests, the Ojainen and Rehtijärvi soils preserved in their sampling moisture were mixed with increasing amounts of wet sediment from Liedonperä CW (Fig. 4) and incubated for three weeks at a moisture content of 35% at

room temperature. The proportion of sediment in these mixtures was 0 (control), 1, 2, 5, 7.5 and 10% of fresh volume. In addition, a mixture of 50% sediment in soil was prepared for the Q/I experiment. Each mixture had three replicates, each with a total volume of 0.9 l. The mixtures were stirred lightly with a spoon and water lost through evaporation was replaced twice a week.

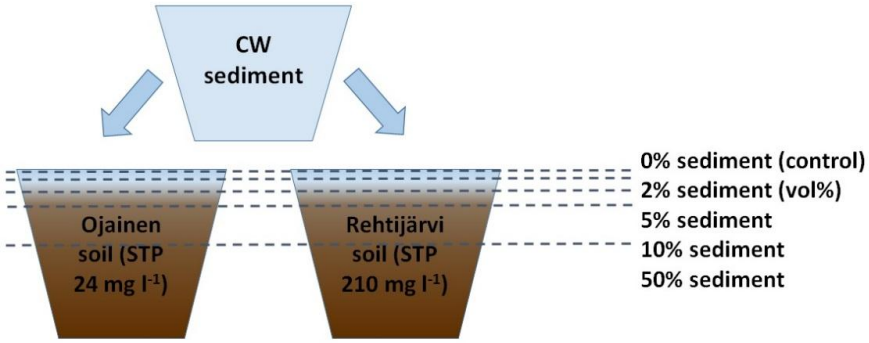



Figure 4. Study design for the soils and CW sediment in the rainfall simulation. Ojainen and Rehtijärvi soils were mixed with an increasing amount of Liedonperä CW sediment.

*Quantity/intensity experiment*

A quantity/intensity (Q/I) test was applied to the incubated soil-sediment mixtures used in the rainfall simulation study to evaluate P sorption or desorption. The Q/I test was performed in triplicate for the mixtures containing 0, 1, 2, 5, 10 and 50% (fresh volume) sediment. After incubation, 1 g of air-dried soil-sediment mixture was shaken at 21°C with 50 ml P solution on an orbital shaker for 30 min, allowed to equilibrate for 16 h, and shaken again for 15 min. The suspensions were then centrifuged (15 min, 3846×*g*) and passed through 0.2-µm Nuclepore membranes (Whatman). The P concentrations in the filtrates were analysed with the molybdenum blue method of Murphy and Riley (1962) using a spectrophotometer (Ordior UVmini-1240 UV-VIS). Phosphorus solution concentrations were 0.0, 0.1, 0.2, 0.5, 1.0, 2.0, 4.0, 6.0 and 8.0 mg $l^{-1}$ for the Ojainen mixtures with P as $KH_2PO_4$ in $H_2O$ (i.e. with no supporting background electrolyte). Initial P concentrations used for Rehtijärvi were 0.0, 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, 15.0 and 20.0 mg $l^{-1}$. The two soils had different P concentrations because of the large difference in their soil test P (STP) concentrations. Initial P concentrations should cover the range from P desorption to a P saturated state where the amount of maximum sorption is achieved in the tested soils. The amount of sorbed or desorbed P (Q) was calculated as the difference between the initial concentration ($I_0$) and the equilibrium concentration (I), multiplied by the solution-to-soil ratio (R):

$$Q = (I_0 - I) \times R \quad (6)$$

A modified Freundlich adsorption equation was then fitted by minimising the sum of squares for parameters a, b and q:

$$Q = a \times I^b - q \quad (7),$$

where Q and I are as in Eq. (6), a and b are fitting parameters and q is the amount of readily desorbable P, when I approaches zero. Using the fitted sorption curves, solution P concentration at which no net sorption or desorption occurs (i.e. equilibrium P concentration, $EPC_0$) and the slope of the Q/I graph at $EPC_0$ for P buffering capacity ($PBC_0$) were estimated.

*Simulated rainfall*

Incubated soil-sediment mixtures were transferred into percolation water collectors. These consisted of 0.15-m diameter cylinders equipped with a tube that allowed percolating water to be collected in plastic bottles. To prevent blockages in the collector tubes, the bottom of each collector was fitted with a nylon filter (1-mm mesh size) overlain by a 1-cm layer (0.15 $dm^3$) of coarse quartz sand rinsed with deionised water and another nylon filter at the top of the sand layer. A 5-cm layer of soil–sediment mixture was then added and slightly compacted in the collector cylinder. The samples were moistened with deionised water to close to field capacity, and allowed to stand overnight before the simulated rainfall event.

The simulated rainfall was applied using a stationary drip-type rainfall simulator in the laboratory (Uusitalo and Aura, 2005). The drip fall height was 2.15 m. Randomised triplicate samples (nine at a time) were set on a 1-$m^2$ stand under the simulator. Rainfall intensity was set to approximately 5 mm $h^{-1}$ with deionised water. Percolating water from each collector was sampled every 100 ml, the total volume being 300 ml (representing batches I, II, and III). The time needed for 300 ml percolation varied between four and 6.5 h per sample. Once the 300-ml water volume was obtained, the sample was removed from the rainfall simulator. The total amount of simulated rain applied was 17 mm, which corresponds to a single rainfall event in southern Finland with a return period of two years, as given by the Finnish Meteorological Institute.

*Water analyses*

Total P and dissolved reactive P were analysed in each of the 100-ml percolation water samples. Particulate P was calculated as the difference between TP and DRP. Total P was analysed from unfiltered samples digested in an autoclave with $K_2S_2O_8$ and $H_2SO_4$ in 120°C, 100 kPa, for 30 min. Subsamples for DRP analyses were filtered through 0.2-µm Nuclepore membranes (Whatman). Phosphorus concentrations were measured with a QC Autoanalyser (Lachat) using the method of Murphy and Riley (1962) with ascorbic acid as the reducing agent. The DRP analysis was performed immediately after collection of the water samples, and the TP analysis was performed after all samples had been

collected. Electrical conductivity and pH of the percolation water were determined with a Mettler Toledo multiparameter meter (Mettler-Toledo, LLC, Columbus, OH, USA).

## 3.4 Quality control of analyses

The chemical analyses were mainly performed in the laboratory of the Natural Resources Institute of Finland in Jokioinen, with some additional analyses in the laboratory of Environmental Soil Sciences at the Department of Food and Environmental Sciences, University of Helsinki. Calibration of all devices was performed according to manufacturers' instructions. All measurements were made on independent replicates, the number of which is given in the method descriptions and in Table 2. Blank samples were included for all soil extraction and water sample measurements. In all soil analyses described in section 3.3.2 and also in the LECO determination of the total C, N and S content, in-house reference materials (local reference soils) were included.

For colorimetric P analyses of the water samples, checks using one standard solution (selected to match concentrations in the samples) as every 30th sample was run, and all standard solutions were analysed as samples before and after the sample runs. Every sample was analysed twice (as pseudo-replicates) and a 5% maximum difference in concentration allowed for a passed sample run.

All standard solutions were analysed as samples before and after the sample runs during ICP determination, and one standard solution was analysed after every 15th sample to detect possible concentration drifts (acceptable range of ±5%). Soil test P (STP) was analysed in a commercial accredited (ISO/IEC 17025) laboratory with their internal QA protocols. A confidence level of 10% was given.

Based on the results in Paper III, the method detection limit (MDL) was determined, i.e. the minimum concentration of a substance that is measurable in a sample. For MDL, the detection limit (DL), i.e. detection limit of the measurement instrument was calculated as:

DL = blank mean + 3*SD of the blanks (8)

MDL values are given in Table 3.

Table 3. Method detection limits (MDL) for certain analyses performed in Paper III.

| Analysis | MDL, mg $l^{-1}$ or mg $kg^{-1}$ | Number of blanks |
|---|---|---|
| Soil test P | 1.5 | DL given by laboratory |
| Alox, Feox | 5.6 | >20 |
| PP | 0.026 | 7 |
| DRP | 0.015 | 7 |
| P fractions | 1.1 for $NH_4Cl$-P; 1.6 $NH_4F$-P; 0.7 NaOH-P; 0.5 $H_2SO_4$-P | 3 |
| P for Q/I plots | 0.053 | 17 |

## 3.5 Statistical analyses

For the parameters analysed, differences in means between soils, fresh sediment and dried sediment within each site were tested with one-way analysis of variance (ANOVA) followed by post-hoc separation of means using the Tukey's test. For analysis of the general trends in the material over all sites, paired tests were performed between soil and fresh sediment, and fresh sediment and dry sediment, using the nonparametric Wilcoxon signed rank test (in Paper I). Significance was taken as $p<0.05$. Statistical analyses were conducted with IBM SPSS Statistics 22.

# 4 Results and discussion

## 4.1 From field to CW – characteristics of the sediment material

### 4.1.1 Clay transport and accumulation

Most agricultural catchments in the study area of southwest Finland are dominated by intensively cultivated fine-textured soils. These catchments are often prone to erosion, and accumulation of clay-sized material was observed in the studied CWs at each of the five sites (Paper I). The CW sediments were fine-textured, consisting of 54–82% clay-sized particles (<0.002 mm) (Table 4). Compared with the catchment soils, the sediments contained 10–80% more clay-sized particles. The enrichment ratio (ER, i.e. the amount of clay in sediment relative to that in topsoil samples) for clay (1.41–1.82) in CWs of larger relative size was greater than that of smaller-sized CWs (1.10–1.20), suggesting higher clay accumulation in larger CWs. This was expected, as the increase in water residence time slows down water velocity in larger CWs and increases the amount of sediment accumulating to the bottom (e.g. Koskiaho, 2006). However, sediment accumulation rates of 22 kg $m^{-2}$ $year^{-1}$ and 40-90 kg $m^{-2}$ $year^{-1}$ have been recorded by Johannesson et al. (2011) and Braskerud et al. (2000) at the inlets of rather small agricultural CWs in Sweden and Norway, respectively. The CW areas in their studies were 2.1 ha or 2% of the catchment in Sweden and 0.03–0.09 ha or 0.03–0.06% of the catchment in Norway. CW sizes in the present study varied between 0.01–0.6 ha or 0.02–5% of the catchment areas (Table 1, p. 18). By way of comparison, average sediment accumulation in a natural-state lake in Finland is <1 kg $m^{-2}$ $year^{-1}$ (e.g. Niemistö et al., 2008).

Topsoil was hypothesised to be the main contributor to erosion at the studied sites, and this was tested by means of $^{137}Cs$ tracer (Paper I). $^{137}Cs$ is firmly attached to soil particles (He and Walling, 1996) and Finland has a clear $^{137}Cs$ signal in topsoils that received a larger $^{137}Cs$ fallout after the Chernobyl nuclear power plant accident in 1986. In clayey Ap-horizon samples, $^{137}Cs$ activities were lower than in the sediment samples at Ojainen and Hovi (Table 4). The other sediments at Liedonperä, Kakskerta and Nautela showed rather similar $^{137}Cs$ activities, but topsoil activities were not measured at these sites. The ERs for $^{137}Cs$ were 1.22 and 1.08 at Ojainen and Hovi, respectively. The $^{137}Cs$ activities of CW sediments were well above the 10 Bq $kg^{-1}$ activity measured for subsoil in southern Finland (Uusitalo et al., 2001) also at the other sites where topsoil $^{137}Cs$ activity was not measured. These results thus suggest that the sediment matter at all sites originated mainly from the topsoil of catchment fields. All of the studied sites had subsurface drainage systems installed, and drainage discharge along with surface runoff carries topsoil as a result of the vertical transport through the soil profile. Transport of soil particles by macropore flow is a typical transport pathway in clay soils (Øygarden et al.,1997; Dils and Heathwaite, 1999; Heathwaite and Dils, 2000; Uusitalo et al., 2001; Gentry et al., 2007; Turtola et al., 2007).

Clay mineralogy was not determined in the study sites but the clay fraction of the Ojainen soil has been found to be rich in mica, vermiculite and also quartz (Yli-Halla et al., 2009), as well as "amorphous material" (Sippola, 1974). This mineralogy of the clay fraction dominates in the entire southern Finland (Sippola, 1974).

Table 4. Clay (<0.002 mm) content, $^{137}Cs$ activity, enrichment ratios for clay and $^{137}Cs$, and acid ammonium oxalate-extractable aluminium ($Al_{ox}$) and iron ($Fe_{ox}$) in the catchment soils and fresh and dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments. Values for oxides are means ± SE.

| Site | | Clay | $^{137}Cs$ | Enrichment ratios for | | $Al_{ox}$ | $Fe_{ox}$ |
|---|---|---|---|---|---|---|---|
| | | % | Bq kg$^{-1}$ | Clay | $^{137}Cs$ | mmol kg$^{-1}$ | mmol kg$^{-1}$ |
| Ojainen | Soil | 45 | 53 | | | 112±9 a | 223±18 a |
| | Fresh sediment | -[1] | - | | | 181±28 a | 253±31 a |
| | Air-dry sediment | 82 | 64 | 1.82 | 1.21 | 292±5 b | 261±3 a |
| Liedonperä | Soil | 35 | - | | | 93±3 c | 191±13 b |
| | Fresh sediment | - | - | | | 124±11 d | 315±48 c |
| | Air-dry sediment | 62 | 69 | 1.77 | - | 186±2 d | 351±4 c |
| Hovi | Soil | 58 | 55 | | | 158±4 e | 203±14 d |
| | Fresh sediment | - | - | | | 145±1 e | 189±3 d |
| | Air-dry sediment | 82 | 59 | 1.41 | 1.07 | 191±3 e | 172±3 d |
| Kakskerta | Soil | 72 | - | | | 159±19 f | 257±16 e |
| | Fresh sediment[2] | - | - | | | 611±75 g | 204±12 e |
| | Air-dry sediment[2] | 79 | 46 | 1.10 | - | 728±4 h | 249±2 e |
| Nautela | Soil | 45 | - | | | 81±3 i | 195±14 f |
| | Fresh sediment[3] | - | - | | | 73±3 i | 206±5 f |
| | Air-dry sediment[3] | 54 | 74 | 1.20 | - | 117±2 i | 225±2 f |

[1] Not measured
[2]Aluminium chloride solution –assisted sedimentation.
[3]Granular ferric sulphate ($Fe_2(SO_4)_3$) –assisted sedimentation.
Different letters for samples (n=2) from each site represent significant differences ($p<0.05$, Tukey's test). Each site was tested separately.

### 4.1.2 Al and Fe (hydr)oxides

Despite the high clay accumulation into the CWs, the fresh sediments only contained somewhat higher concentrations of amorphous Al and Fe (hydr)oxides than the soils in

the field (Table 4), the difference being statistically significant only at Liedonperä and Kakskerta (the latter with Al chemical treating) (Paper I). The non-significant difference of the three other sites may indicate that fine clay particles are not retained in CWs. Sippola (1974, p. 201) determined the mineral composition of subsoil (below 20 cm) of the fine clay fraction (<0.2 μm) and found that the amount of amorphous material was higher (18.4% of weight) than in the coarser clay fraction (0.2–2 μm; 4.5% of weight), and strikingly diminished towards coarser fractions. In this work, the clay fraction (<2 μm) was not further subdivided, so the proportions of the fine and coarser clay and their contributions to Fe and Al (hydr)oxides remain unknown.

Braskerud (2003) showed that fine clay particles from arable land had sedimentation velocities similar to coarse clay or silt, indicating a high degree of aggregation. As a result, an efficient retention of fine clay was also observed at high hydraulic loads (Braskerud, 2002). On the other hand, Ulén (2004) reported that tile drain runoff from agricultural clay soils in Sweden consisted mostly of colloids and fine clay with a theoretical settling velocity of less than 1 cm $day^{-1}$, indicating much lower sedimentation into a wetland in such soils. It seems plausible that finer clay is not effectively retained by the CWs studied in this work, or it is readily re-suspended and flushed out during periods of high flow.

The sediment in the chemical-assisted Nautela CW did not bear any notable traces of $Fe_2(SO_4)_3$ feeding to the inflow, with only slightly higher amorphous Fe (hydr)oxide content in the sediment than in the parent soil (Table 4). Nautela CW has previously been found to have good P retention efficiency (49–84% during a two-year study) during chemical feeding (Uusitalo et al., 2013). The use of $Fe_2(SO_4)_3$ additive can be effective in the formation of new amorphous Fe-hydroxyl species via chemical reactions (Eq. 9). These newly formed Fe (hydr)oxide precipitates have a large surface area and plenty of reactive sites for P sorption (Lijklema, 1980). During ageing, the oxides show higher crystallisation and reduction in surface area for P adsorption (McLaughlin et al., 1981).

$$Fe_2(SO_4)_3 + 6\ H_2O \rightarrow 2\ Fe(OH)_3 + 6\ H^+ + 3\ SO_4^{2-} \quad (9)$$

Formation of amorphous Fe (hydr)oxides in CWs may also occur without additives, as fine-textured eroded soil material is naturally rich in Fe. According to the on-site redox potential readings, the studied sediments were initially at a low redox state that is conducive to the dissolution of Fe(III) (Eq. 10). The occasional introduction of oxygen into the anoxic sediment during high-flow periods, for example, produces new Fe (hydr)oxide surfaces for P sorption (Eq. 11) (Khalid et al., 1977; Jensen et al., 1995; Palmer-Felgate et al., 2011). Fe plays an important role in binding P in CWs.

$$Fe(OH)_3 + 3\ H^+ + e^- \rightarrow Fe^{2+} + 3\ H_2O \quad (10)$$
$$4\ Fe^{2+} + O_2 + 10\ H_2O \rightarrow 4\ Fe(OH)_3 + 8\ H^+ \quad (11)$$

Although the concentration of Al (hydr)oxides was not higher in the sediments than in soils (except at Kakskerta), it can be more stable than Fe (hydr)oxides as a sorption

component for P in sediments of CWs. As Al (hydr)oxides are not redox sensitive, they can maintain the reactivity for P sorption in anoxic conditions. At elevated pH, conditions that may occur in eutrophic waters, Al (hydr)oxides preserve their sorption ability better than Fe (hydr)oxides, because the coordination sphere of Al maintains more $-H_2O$ groups than Fe does. They are more easily replaced by P than -OH groups in oxide surfaces are.

### 4.1.3 Phosphorus content and speciation

Practically equal amounts of TP were measured in the parent soils and sediments, with a range of 975–1450 mg $kg^{-1}$ in the soils and 972–1467 mg $kg^{-1}$ in the sediments (Fig. 5) (Paper I). The mean share of organic P of TP was 27% in the soils and 19% in the sediments (excluding Kakskerta sediment, where chemically assisted sedimentation increased organic P to 45% of TP). In CWs established on mineral soils, organic P content may range from 10 to 50% of the total P (Reddy and DeLaune, 2008). In Sweden, Johannesson et al. (2011) measured a 38% share for organic P of TP in the sediment of an agricultural CW. The lower organic P content in the sediments than the soils of this study suggests that the organic P pool was not transported or retained in CWs, or this fraction was partly mineralised in the wetlands. The rate of organic P mineralisation is strongly regulated by redox conditions. Suspended matter is a significant carrier of organic P as inositol hexaphosphate, and under anoxia it may be rapidly and extensively mineralised as a result of the release of the inositol hexaphosphate molecule from Fe-associated particles upon Fe(III) dissolution at low redox conditions (Suzumura and Kamatani, 1995).

According to Chang and Jackson (1957) fractioning, the $H_2SO_4$-P, i.e. Ca-bound P (assumed to be rather inert apatite-P), showed no statistically significant differences between soils and sediments. The similarity of this supposedly apatite-P pool may suggest that the sediment matter originates in the topsoil of the arable fields in the catchments, in agreement with $^{137}Cs$ analysis. Lukkari et al. (2008) also found a uniform apatite-P concentration through sediment profiles (0–25 cm) in a shallow estuary of the Baltic Sea, where the catchment consisted of 50% arable clayey soil. They concluded that apatite-P was the most stable fraction in the sediment of their study.

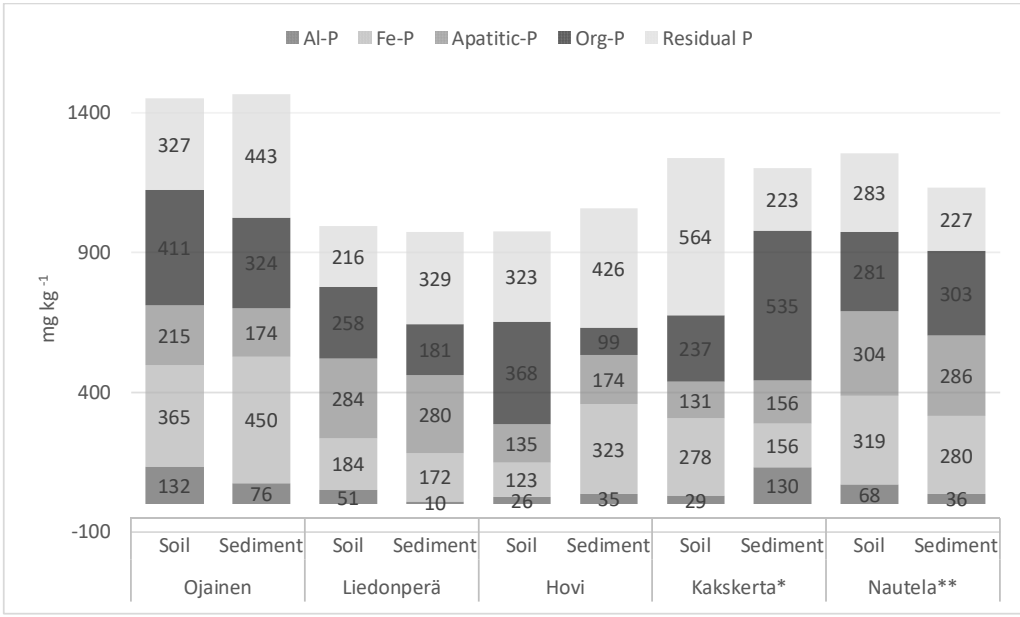



Figure 5. Total phosphorus concentration, Al- and Fe-bound P and apatitic-P from Chang and Jackson P fractions ($NH_4F$-P, NaOH-P, $H_2SO_4$-P, respectively), organic P (Org-P) concentration and calculated residual P content of the catchment soils and the dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments. Values shown are means. *Aluminium chloride solution –assisted sedimentation. **Granular ferric sulphate ($Fe_2(SO_4)_3$) –assisted sedimentation.

The most striking differences between the studied soils and sediments were found in the quantities of Al- and Fe-bound P (Fig. 5). In non-calcareous agricultural soils (cited studies are from Finland and Sweden), P added as fertiliser is generally retained to the topsoil on Al and Fe (hydr)oxides ($NH_4F$-P and NaOH-P, respectively), and the amount decreases with depth (Hartikainen, 1989; Peltovuori, 2006; Eriksson, 2016). In the studied soils, the sum of metal oxide-bound P was the largest inorganic P pool comprising 15–34% of TP, a range typical for Finnish agricultural soils (e.g. Peltovuori, 2006; Soinne et al., 2011). These fractions turned out to be clearly affected by transport from the soil to the CW and storage in the CW. The most loosely bound P pool, $NH_4Cl$-extractable P, was negligible (<1 mg $kg^{-1}$) in both soils and sediments.

Pairwise statistical testing over all sites suggested that Al-bound P concentrations were significantly lower in fresh sediments than in soils, when the Kakskerta CW was excluded from the testing. During transport, settling and storage at the bottom of CWs, the ambient solution surrounding the eroded soil (i.e. runoff water, overlying water or pore water in CW) becomes lower in the dissolved P concentration than was present in the initial soil solution, and a considerable fraction of Al-bound P may be depleted (Hartikainen, 1982; Liikanen et al., 2004). In the soils studied, depletion of readily soluble P most probably occurs from particle surfaces and is readily available for algal production (Ekholm, 1994) or for macrophytes provoking eutrophication.

Kakskerta and Hovi stand out as CWs with abundant Al-bound P (Paper I). The Kakskerta sediment was affected by the Al chemical feed to the incoming water, an obvious reason for the increase in Al-associated P. At Hovi, Al-bound P was also clearly higher in the sediment than in soil, but without inputs of Al chemicals. The most remarkable difference from the other sites was the very large size of Hovi CW, 5% of the catchment area, resulting in a longer water residence time. This would promote particle settling and the reaction time of dissolved P to associate with oxide surfaces in the sediment. As in the present study, Liikanen et al. (2004) also demonstrated the important role of Al (hydr)oxides in retaining P at Hovi CW.

The Fe-bound P (NaOH-P) in the sediment was substantially greater than in the parent soils at three of the sites, while it was approximately equal to the parent soil content at Liedonperä (Fig. 5) (Paper I). Fe-bound P represented 31% of TP at both Ojainen and Hovi sediments, compared to 25 and 13% in the parent soils, respectively. Fe-bound P was lower in the sediment at Kakskerta than in the soil, probably because the Al feed at the CW inlet had added a large Al oxide mass into the Kakskerta sediment over the years. Freshly settled Al adsorbs P from the Fe-associated pool in lakes where Al chemicals have been used in restoration (Rydin and Welch, 1998; Lewandowski et al., 2003). Thus, changes in the P saturation of one sorption component (Al or Fe (hydr)oxide surface) likely affects the P saturation of the other component (see Hartikainen, 1982; Hartikainen et al., 2010). Iron (hydr)oxides can be assumed to be partly dissolved and reprecipitated, as redox conditions shift periodically in the bottom of the CWs. Once the sediment turns anoxic, P saturation of Al (hydr)oxides can be thought to increase as a result of the solubilisation of Fe-P associations.

Lastly, summing the Chang and Jackson (1957) inorganic P fractions resulted in 44% and 47% mean recovery of TP in the soils and sediments, respectively. Peltovuori (2006) also reported rather low recovery in two clay field topsoils (41% and 47% of TP). The remaining P, besides organic, is thought to occur as reductant-soluble and occluded forms of P. These unrecovered P fractions, however, are assumed to represent P with low bioavailability, whereas the most readily soluble P fractions are well represented in the first fractions ($NH_4Cl$-P and $NH_4F$-P) of sequential extractions.

### 4.1.4 P sorption capacity and degree of P saturation

Fresh sediments had somewhat higher P sorption capacities (PSC) than their parent soils (Table 5), except at Hovi where PSC was lower in the fresh sediment than in soil, although not statistically significantly. The highest PSC value was found in Kakskerta soil, which had the highest clay content (72%) of the studied fields. Attributable also to the Al chemical treatment at Kakskerta, sediment PSC was twice that in the parent soil.

The DPS indices suggested that Fe (hydr)oxides were more saturated with P ($DPS_{Feox}$, calculated as NaOH-P/$Fe_{ox}$) than Al (hydr)oxides ($DPS_{Alox}$, $NH_4F$-P/$Al_{ox}$) in all sediments and soils. The combined index $DPS_{\Sigma}$ (($NH_4Cl$-P+$NH_4F$-P+NaOH-P)/PSC) was smaller in the fresh sediments of Ojainen, Liedonperä and Kakskerta than in the soils of these sites (Table 5). Although the PSC or DPS indices did not show parallel trends between the soils

and sediments, the affinity of Al and Fe (hydr)oxide surfaces for P sorption may be greater in the sediments (Papers I, II and III). Thus, the properties of oxide surfaces (e.g. crystallinity) and the ambient conditions, as discussed earlier (in 4.1.2), play a key role, as the affinity of these substrates sets the concentration of P in aquatic systems such CWs.

Table 5. Phosphorus sorption capacity (PSC), degree of P saturation of oxides ($DPS_{Alox}$, $DPS_{Feox}$), the sum of $NH_4Cl$-, $NH_4F$- and NaOH-extractable Chang and Jackson P fractions ($P_\Sigma$) and P saturation calculated as $P_\Sigma$ / PSC ($DPS_\Sigma$) in the catchment soils and fresh and dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments. Values are means.

| Site | | PSC | $DPS_{Alox}$ | $DPS_{Feox}$ | $P_\Sigma(NH_4Cl, NH_4F, NaOH)$ | $DPS_\Sigma$ |
|---|---|---|---|---|---|---|
| | | mmol $kg^{-1}$ | % | % | mmol $kg^{-1}$ | % |
| Ojainen | Soil | 168 | 7.6 | 10.6 | 16 | 9.6 |
| | Fresh sediment | 217 | 2.5 | 13.9 | 20 | 9.2 |
| | Air-dry sediment | 277 | 1.7 | 11.1 | 17 | 6.1 |
| Liedonperä | Soil | 142 | 3.5 | 6.2 | 8 | 5.4 |
| | Fresh sediment | 220 | 1.0 | 3.9 | 7 | 3.1 |
| | Air-dry sediment | 269 | 0.3 | 3.2 | 6 | 2.2 |
| Hovi | Soil | 181 | 1.1 | 3.9 | 5 | 2.7 |
| | Fresh sediment | 167 | 3.9 | 10.7 | 13 | 7.8 |
| | Air-dry sediment | 182 | 1.2 | 12.1 | 12 | 6.4 |
| Kakskerta | Soil | 208 | 1.2 | 7.0 | 10 | 4.8 |
| | Fresh sediment[1] | 408 | 1.9 | 5.4 | 11 | 2.8 |
| | Air-dry sediment[1] | 489 | 1.2 | 4.0 | 9 | 1.9 |
| Nautela | Soil | 138 | 5.4 | 10.6 | 12 | 9.1 |
| | Fresh sediment[2] | 140 | 3.2 | 13.8 | 15 | 11.0 |
| | Air-dry sediment[2] | 171 | 2.0 | 8.0 | 10 | 6.0 |

[1] Aluminium chloride solution –assisted sedimentation.
[2] Granular ferric sulphate ($Fe_2(SO_4)_3$) –assisted sedimentation.

### 4.1.5 C, N and S content in soil and sediment

Some accumulation of total C (Tot-C) and N (Tot-N) was observed in the sediments, particularly in the CWs where sedimentation was chemically assisted (Table 6). The addition of Fe and Al salts (at Nautela and Kakskerta, respectively) most likely resulted

in flocculation of fine particles and dissolved humus, and settling of the particulates during low-flow periods. This resulted in higher C and N concentrations than in the parent soils. A strong positive correlation was found between C and N, as the $r^2$ for soils and sediments was 0.97 and 0.99, respectively. The C/N ratio at the sites without chemical additives was somewhat higher in the soils than in the sediments. Again, rather similar ratios indicate field origin of the organic matter in sediments.

Accumulation of S in all CW sediments was observed, despite the relatively S-poor agricultural topsoils in their parent catchments (Papers I, III). During sediment sampling, Eh values (-21 to +105 mV) suggested anoxic conditions, which were also evidenced by the smell of hydrogen sulphide ($H_2S$), along with black spots that were presumably indicative of sulphides.

Sulphate likely originates from the mineralisation of organic matter in CWs, or is transported from fields with incoming water, from which it can diffuse down into the reduced sediment surface layer and be reduced to sulphide. Ambient conditions in sulphate reduction are near neutral pH and Eh –200 to 0 mV. Both of these preconditions were filled, as pH levels of 6.3–7.3 (the pH at Nautela was 5.2 due to acidic chemical addition) and redox readings of -21 to +105 mV were recorded from the studied sediments. Sulphide can further react with Fe(II) and precipitate as iron sulphides (FeS) in sediments (Berner, 1984; Lehtoranta et. al, 2009). The $SO_4^{2-}$ concentration of the overlying CW water at Ojainen was 10 mg $l^{-1}$ (not measured at the other sites), thus higher than the average sulphate concentration (3.6 mg $l^{-1}$) in Finnish lakes (n=171, Mannio and Vuorenmaa, 1995). Sulphate supposedly originates in fertilisers. The importance of fertilisers as a source was emphasised by Bates et al. (2002), who measured (using stable isotope signatures) an accumulation of $SO_4^{2-}$-S and Tot-S in sediments adjacent to agricultural areas receiving water with sulphate concentration, up to 48 mg $l^{-1}$, in the Florida Everglades.

Especially during summer months, redox conditions in agricultural CWs might fluctuate widely as increased temperature enhances microbial activity that may rapidly consume oxygen at the sediment-water interface. While alkalinity is produced in the reactions of bacterial sulphate reduction, which may elevate the pH up to 2 units (Ponnamperuma, 1972), drying induces an opposite reaction. A decline in pH by 0.6–2.2 units upon drying (from pH 5.2–7.3) was measured for the sediments in this study (Paper I). This drop was associated with high $SO_4^{2-}$-S concentrations found in dried sediments, which suggests sulphide oxidation (Papers I, III). Equations (12) and (13) show Fe sulphide (FeS and $FeS_2$) oxidation reactions producing $SO_4^{2-}$ -ions and acidity ($H^+$), along with new Fe oxide surfaces as a solid product.

$$FeS + 2.25\ O_2 + 2.5\ H_2O \rightarrow Fe(OH)_3 + SO_4^{2-} + 2\ H^+ \quad (12)$$

$$FeS_2 + 4.25\ O_2 + 2.5\ H_2O \rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 2\ H^+ \quad (13)$$

A considerably lower ratio of C/S in the sediments than soils was found. The low ratio of $SO_4^{2-}$-S/Tot-S in the agricultural soils indicated that S was mainly organic, but

significantly higher concentrations of inorganic S was found in the (dried) sediments at Ojainen, Hovi and Nautela, presumably due to sulphide oxidation. C and S correlated well in both the soils and sediments, $r^2$ being 0.89 for the soils and 0.91 for the sediments. At Kakskerta, the Tot-S content was 4–6 times larger than at the other sites (also high $SO_4^{2-}$-S and Tot-C), probably as a result of the geological history of the soil (Paper I). The considerably high Tot-S concentration and the location on Kakskerta island points towards acid sulphate soil features (Kivinen, 1950). The parent sediments of these presumably acid sulphate soils were formed during the Litorina Sea stage of the Baltic Sea.

Table 6. Total carbon (Tot-C), total nitrogen (Tot-N), total sulphur (Tot-S), sulphate-S ($SO_4^{2-}$-S) and ratios of Tot-C to Tot-N, Tot-C to Tot-S and $SO_4^{2-}$-S to Tot-S of the catchment soils and the dry Ojainen, Liedonperä, Hovi, Kakskerta and Nautela sediments. $SO_4^{2-}$-S results are given as means ± SE.

| Site | | Tot-C | Tot-N | Tot-S | $SO_4^{2-}$-S[1] | C/N | C/S | $SO_4^{2-}$-S/Tot S |
|---|---|---|---|---|---|---|---|---|
| | | % | % | % | mg kg$^{-1}$ | | | |
| Ojainen | Soil | 2.8 | 0.19 | 0.03 | 17±0 a | 15 | 109 | 7 |
| | Sediment | 3.6 | 0.34 | 0.13 | 877±4 b | 11 | 28 | 67 |
| Liedonperä | Soil | 1.7 | 0.12 | 0.02 | 20±0 c | 14 | 90 | 10 |
| | Sediment | 1.3 | 0.12 | 0.14 | 98±1 d | 11 | 9 | 7 |
| Hovi | Soil | 1.8 | 0.14 | 0.02 | 20±0 e | 13 | 76 | 8 |
| | Sediment | 2.2 | 0.19 | 0.05 | 227±1 f | 12 | 42 | 44 |
| Kakskerta | Soil | 4.6 | 0.37 | 0.12 | 136±9 g | 13 | 39 | 11 |
| | Sediment[2] | 15.0 | 0.95 | 0.64 | 449±2 h | 16 | 23 | 7 |
| Nautela | Soil | 1.8 | 0.15 | 0.02 | 20±0 i | 11 | 80 | 9 |
| | Sediment[3] | 5.2 | 0.42 | 0.10 | 284±2 j | 12 | 52 | 28 |

Different letters for $SO_4^{2-}$-S values of soil and sediment (n=3) represent significant differences ($p<0.05$, Tukey's test). Each site was tested separately.
[1]$SO_4^{2-}$-S was extracted with acidic ammonium acetate (0.5M acetic acid, 0.5M ammonium acetate, pH 4.65, AAAc) according to the Finnish agronomic soil testing protocol (Vuorinen and Mäkitie, 1955) from dried sediments
[2]Aluminium chloride solution –assisted sedimentation.
[3]Granular ferric sulphate ($Fe_2(SO_4)_3$) –assisted sedimentation.

*Vivianite formation*

One possible mechanism of P retention, or rather P burial in CW sediments, is the formation of vivianite ($Fe_3(PO_4)_2 \times 8H_2O$). Vivianite is an authigenic Fe(II)-phosphate mineral, and the most common stable iron phosphate mineral in sedimentary environments (Nriagu, 1972). Although vivianite formation was not studied in these sediments, this possible mechanism arose when surveying the literate. Vivianite is formed under mildly reduced non-sulfidic conditions, where organic matter supply and anaerobic

degradation are high and, consequently, high concentrations of $Fe^{2+}$ and soluble reactive P are available in pore water (Nriagu, 1972; Roden and Edmonds, 1997). Eroded soil material from clayey agricultural fields is relatively rich in Fe, readily available in P and organic matter, and conditions in CWs are seasonally favourable to vivianite formation. This leads to an interesting question: can vivianite be formed in agricultural CWs? By the extraction procedures performed in this work, vivianite precipitate would probably have been extracted by $H_2SO_4$ (acid-soluble P from Fe(II)/Fe(III) mineral phases (Postma, 1993)), but the identification of vivianite-related P in this fraction was not performed. Future research concerning the preconditions for vivianite formation and occurrence in CWs are needed. Because vivianite is stable in reduced conditions, the burial of P by vivianite in sediments would improve long-term immobilisation of P and restrain occasional P fluxes from reduced CW sediments to overlying water. When sediment is dredged, vivianite oxidation will begin.

The formation of vivianite as a long-term P retention mechanism in sediment systems has been largely ignored until recent years (Rothe et al. 2016). O'Connell et al. (2015) reported yearly fluxes of 26% of TP to be found as vivianite in lake sediment in Denmark. Rothe et al. (2014) emphasised the role of vivianite formation (with artificial Fe addition), which enabled a lake to recover from its former eutrophic state to a mesotrophic level.

### 4.1.6 Desorbable and redox-sensitive P

The phosphorus found in fresh sediments was abundantly extractable with anion exchange resin (AER-P, Fig. 6) (Paper I), which positively correlates with algal assays (Uusitalo and Ekholm, 2003). The amount of AER-P in the fresh sediments was up to 10-fold compared to the parent soils at Ojainen and Hovi, and also showed a significant difference at other sites ($p = 0.017$). Chemical reduction by BD extraction showed that large reserves of redox-sensitive P (Fe-bound P) occurred in the sediments (Fig. 6), representing 23–48% of TP (excluding Kakskerta, where Al chemical treatment had diminished the BD-P fraction). Thus, the redox state during sampling, even if anoxic, had not entirely exhausted the redox-labile P pool in sediments.

To sum up the redox sensitivity of Fe-bound P in the sediment and some results of this "From field to CW" section, anoxic conditions and reducing reactions in CW sediments might result in the mobilisation of Fe-bound P from the large redox-sensitive reserves into the water phase, and some of this P is likely transported further out of the CW as dissolved P. The organic matter loading and decaying vegetation in CW promote the development of anoxic conditions. This may turn CW to act as a "P pump" from its primary role as a P sink. The net release of dissolved reactive P from CWs have been reported by many authors (Fisher and Reddy, 2001; Braskerud et al., 2005; Tanner et al., 2005; Palmer-Felgate et al., 2011; Kynkäänniemi et al., 2013). In Sweden, a net loss of TP from CW was observed in December 2010, with low flow during the ice-covered period and the relative TP retention being -28% during this month (the quantity being less than 1 kg TP $ha^{-1}$ of the wetland) (Kynkäänniemi et al., 2013). Also Braskerud et al. (2005) emphasised the high hydraulic loading rate as an important factor for keeping the layer above the

sediment oxidized in cold temperate regions, as stagnant periods lower the redox state and occasional P leakage would occur. Tanner et al. (2005) reported that a wetland (1% of catchment area) treating drainage waters from a dairy cow pasture in New Zealand generally released more TP and DRP than it received during a two-year period. Net DRP release (~80% of TP) may have occurred as a result of mineralisation and/or redox changes in newly flooded agricultural topsoils, despite a considerably high P retention capacity of the wetland soils as measured in the laboratory (Tanner et al., 2005).

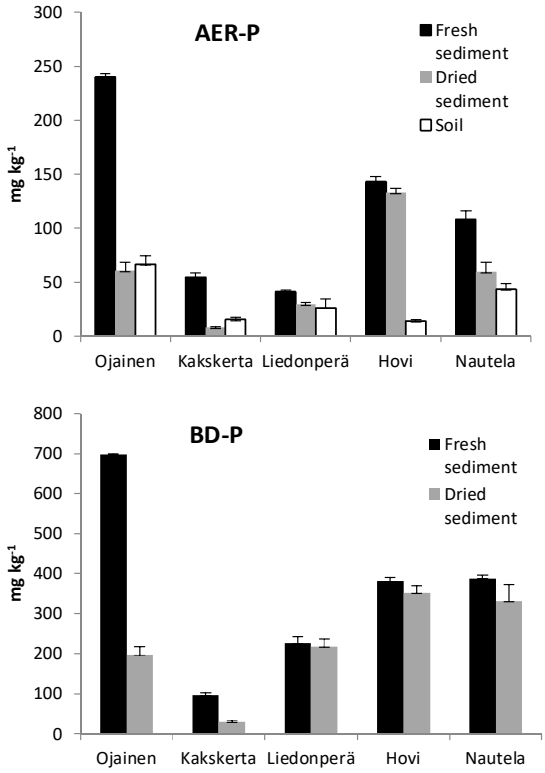



Figure 6. Anion exchange resin-extractable phosphorus (AER-P) of the fresh and dried sediments and catchment soils and bicarbonate dithionite-extractable P (BD-P) of the fresh and dried sediments of Ojainen, Liedonperä, Hovi, Kakskerta and Nautela. Results are given as means (n=3 for AER-P and n=4 for BD-P) ± SE (error bars). At Kakskerta, aluminium chloride solution and at Nautela granular ferric sulphate ($Fe_2(SO_4)_3$) –assisted sedimentation were applied.

## 4.2 Drying and re-oxidation of sediment – effects linked to dredging and land application

Anoxic sediment is brought into an oxic environment during dredging, and drying and re-oxidation will change the properties of the sediment material. A pairwise comparison of all the sites between the fresh and dried sediments showed a significant decline in AER-P ($p$=0.047) upon drying (Fig. 6). This may be due to the fact that the sediment material

was richer in oxides after drying than in the fresh state. In particular, the content of Al (hydr)oxides increased by 32–61% after sediment drying (chemically treated sites excluded) (Table 4, p. 32). Some increase in Fe (hydr)oxides after drying was also observed, although levels were statistically non-significant, but their high affinity for P as newly formed sorption sites has been emphasised in earlier discussion (4.1.2 and 4.1.5). During sediment drying, the newly formed Al and Fe oxides are assumed to originate in the drying-induced breakdown of Al and Fe complexes of organic matter, which thereby increases the degree of P adsorption (Bartlett and James, 1980; Haynes and Swift, 1985; Peltovuori and Soinne, 2005). In addition, under flooded-drained conditions in California soils Sah et al. (1989) showed an increase in concentration of amorphous Fe at the expense of more crystalline forms, thus increasing P sorption. The phenomenon contributed to a decreased redox potential in the flooded soil. Sulphide oxidation may also contribute in the case of a slight increase in Fe (hydr)oxide concentration.

Drying decreased BD-extractable P in all sediments (Fig. 6), but within-site difference was significant only at Ojainen. The BD-extraction is capable of dissolving P even from crystalline Fe (hydr)oxides, which suggests that BD-extraction was incomplete in dried sediments. Hard aggregates of dried sediment may have needed longer or repeated extraction for required reaction to dissolve the large P reserve that was bound to Fe oxides.

The fraction of $NH_4F$-P was found to not differ between fresh and dried sediments, but drying of the sediments significantly ($p = 0.012$) decreased the NaOH-P pool. This may be due to the method used, because the increase of the "inert" $H_2SO_4$-P fraction was observed in the sequential procedure, which most likely results from the non-recovered NaOH-P fraction (Paper I). As already mentioned, sediment drying allows the formation of a more ordered crystalline structure (McLaughlin et al., 1981; Sah et al., 1989), which was possibly not recovered during the NaOH extraction in the procedure used.

As an consequence of the increase in Al (hydr)oxides after drying, $DPS_{Alox}$ was smaller in the dried sediments. When the DPS of $Al_{ox}$ and $Fe_{ox}$ was combined in the same index ($DPS_{\Sigma}$), the dried sediments were less saturated with P than the fresh sediments or parent soils (except Hovi) (Table 5, p. 37). This indicates that applying dredged sediments to soils would add to soil stocks of reactive Al and Fe (hydr)oxides (Papers II, III).

## 4.3 Amending soil with sediment

### 4.3.1 P sorption-desorption measures after addition of sediment to soil

The effect of CW sediment addition into the soil did not stand out in the chemically determined soil properties that reflect P sorption ($Al_{ox}$, $Fe_{ox}$, or $DPS_{\Sigma}$) until the highest sediment addition rate (50 vol-%) was used (Paper III). However, substantial reductions in the Q/I plot characteristics were observed already at the 2% to 5% sediment addition rates. Equilibrium P concentration ($EPC_0$) turned out to be the most sensitive measure used when assessing the effects of sediment addition into soil. Amending two soils (Ojainen silty clay and Rehtijärvi sandy loam, Paper III) with P-depleted Liedonperä CW sediment appeared to immobilise soil P. The two soils, which had a 10-fold difference in

their agronomic P test values (24 and 210 mg $P_{Ac}$ $l^{-1}$ for Ojainen and Rehtijärvi, respectively), had a more than 60-fold difference in their $EPC_0$ values (0.69 and 44.3 mg $l^{-1}$ for Ojainen and Rehtijärvi, respectively) (Table 7). The $EPC_0$ value for both soils decreased steadily with an increasing sediment addition rate, but at a clearly different pace. The $EPC_0$ value of Ojainen was halved with the addition of 10% sediment, whereas the $EPC_0$ value of Rehtijärvi soil was halved already at the 5% addition rate. For both soils, adding 50% sediment resulted in the same low $EPC_0$ value (0.05 mg $l^{-1}$). As an indication of the P sorption affinity at $EPC_0$, the estimated P buffering capacity ($PBC_0$) for the Ojainen soil increased by 45% at the 2% sediment addition rate, but remained at this same level at the 5% and 10% rates (Table 7). Sediment application rates of 2% or 5% appeared to only have a small effect on the actual $PBC_0$ values for Rehtijärvi soil, but 50% sediment application substantially increased $PBC_0$ at both soils.

Mixing the sediment into soil clearly increased their tendency to retain P, while it also increased P buffering and depressed P solubility. Reddy et al. (1995) reviewed several Q/I studies on the P sorption properties of wetland and stream sediments in Lake Okeechobee Basin (Florida, US) and reported that wetland sediments were capable of retaining as much as an additional 54% of TP by Fe and Al oxides (or calcium carbonate). As concluded in Papers I–III, Al (hydr)oxides are mostly increased due to drying the CW sediments and newly formed Fe (hydr)oxides have a high affinity for P adsorption, and are thus efficient at declining soil soluble P (e.g. Jensen et al., 1995). As a conclusion, sediment application in soils can have a noticeable influence on immobilising soil P.

Table 7. Equilibrium P concentration ($EPC_0$) and P buffering capacity at equilibrium P concentration ($PBC_0$) of the soil-sediment mixtures with 0%, 2%, 5%, 10% and 50% sediment addition rates for Ojainen (silty clay, SIC) and Rehtijärvi (sandy loam, SL). The two soils differ in their agronomic P test values, Ojainen and Rehtijärvi having 24 and 210 mg $P_{Ac}$ $l^{-1}$, respectively.

| Soil mixture | Sediment addition rate | $EPC_0$ | $PBC_0$ |
|---|---|---|---|
| | % (v:v) | mg $l^{-1}$ | l $kg^{-1}$ |
| *Ojainen, silty clay* | | | |
| SIC_0 (control) | 0 | 0.69 | 19.8 |
| SIC_2 | 2 | 0.59 | 28.8 |
| SIC_5 | 5 | 0.44 | 26.4 |
| SIC_10 | 10 | 0.36 | 28.8 |
| SIC_50 | 50 | 0.05 | 54.7 |
| *Rehtijärvi, sandy loam* | | | |
| SL_0 (control) | 0 | 44.3[1] | 2.4 |
| SL_2 | 2 | 38.6[1] | 1.0 |
| SL_5 | 5 | 20.2 | 2.0 |
| SL_10 | 10 | 10.0 | 13.5 |
| SL_50 | 50 | 0.05 | 33.2 |

[1]Extrapolated value

### 4.3.2 Two-point-method for determining $EPC_0$'

In this work, the Q/I analyses were performed as a complementary analysis to the other sorption-desorption experiments: with a rainfall simulation study, $EPC_0$ estimates were determined with a fitted curve of the modified Freundlich adsorption equation with 9–11 different P solution concentrations (Paper III), and the pot experiment was supported by $EPC_0$'estimates determined with a simple linear equation with two different P solutions (Paper II).

A simple two-point P sorption test was performed to evaluate $EPC_0$' values of soil-sediment mixtures by linear regression. At low P concentrations (at least <0.3–0.5 mg $l^{-1}$) a linear relationship is often found between sorbed or desorbed P, and the P concentration in solution after equilibrium (Hartikainen, 1979; House and Denison, 2000; Lucci et al., 2010). In Fig. 7 the comparative estimates for $EPC_0$ and $EPC_0$' for the soil-sediment mixtures are shown with both methods.

The two-point method appeared to overestimate the $EPC_0$' value of soils without sediment amendments. As the share of sediment (and P adsorption surfaces) in the soils increased, the estimates became more similar to the ones obtained with the modified Freundlich equation. The similarity of the decreasing pace of the curves and end points, i.e. the highest sediment addition rates, were confirmed with an F-test. The two-point method appeared to be a practical procedure for evaluating P affinity of the soil-sediment mixtures and the direction of $EPC_0$ change. Although $EPC_0$' estimates should not be considered equivalent to the $EPC_0$ values determined by a modified Freundlich sorption

isotherm method, this turned out to be a good method for comparing these mixtures. The procedure saved time and reagents compared to the "full" extraction series. If accurate estimates for $EPC_0$ are needed, the modified Freundlich equation method with a larger series of P solutions would be the recommended procedure.

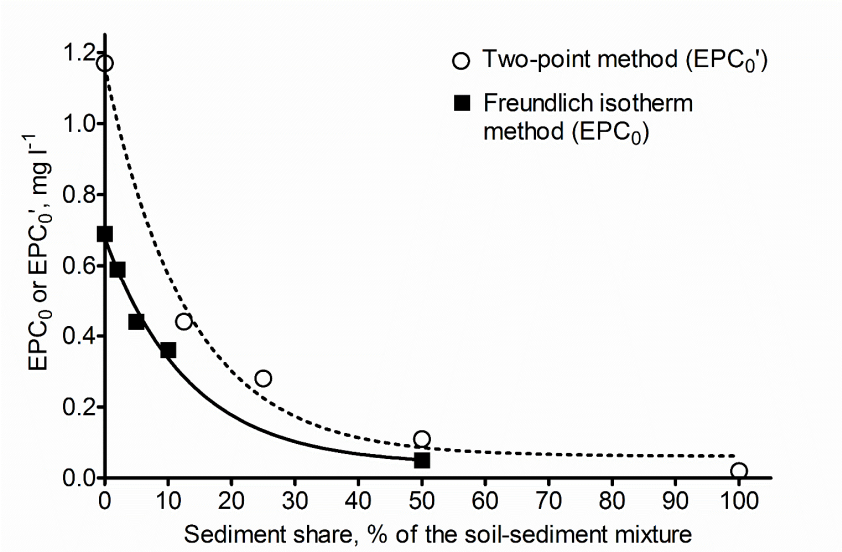



Figure 7. A comparison of two methods: equilibrium P concentrations ($EPC_0$) determined by a modified Freundlich adsorption equation ($EPC_0$) and a two-point sorption method ($EPC_0$') of soil-sediment mixtures. NOTE: Ojainen soil and Liedonperä sediment are the mixture components for $EPC_0$, while Ojainen soil and Ojainen sediment are mixed for $EPC_0$'.

### 4.3.3 P fractions of soil-sediment mixtures

Amending soils with CW sediment had variable effects on the P fractions. Fig. 8 a) and b) show Chang & Jackson P fractions determined from the mixtures after three-week incubation, but the size of the P fractions based on the percentage relations of soil and sediment in the mixtures are also shown. This comparison was performed to explore whether an introduction of new sorption surfaces by sediment amendment could show a detectable shift between P fractions from an initial state during the three-week time period.

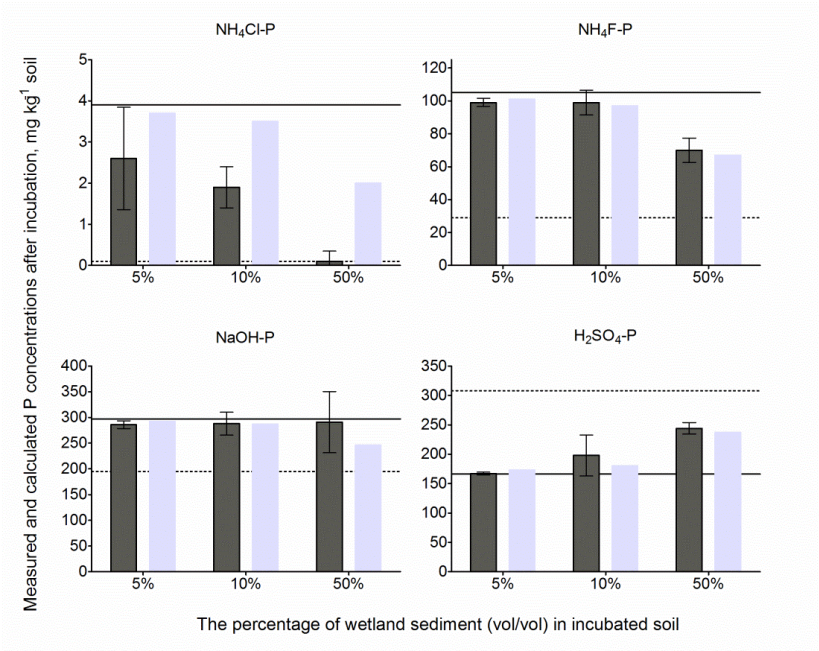
Sediment amendment decreased the readily available $NH_4Cl$-P at Ojainen, although not significantly. However, this fraction was higher when calculated from the concentrations in the mixed-in soil and sediment than the result of the chemical fractionation of the actual mixture (Fig. 8 a). Moreover, sediment additions in the soil caused a significant decrease in $NH_4Cl$-P at all addition rates (for all $p<0.001$) in the coarser Rehtijärvi soil (Fig. 8 b) with excessive soil test P (210 mg $P_{Ac}$ $l^{-1}$). This outcome suggests a shift in $NH_4Cl$-P to other less soluble fractions. A shift to the NaOH-P (Fe-

bound P) pool particularly stands out, whereas the $NH_4F$-P (Al-bound P) pool remained unchanged.

The fact that the decrease in easily soluble P is detectable as an increase in Fe-bound P and not the Al-P pool is interesting because Al (hydr)oxide surfaces were almost P depleted compared to the Fe (hydr)oxides, and the number of sorption sites on Al was found to increase due to sediment drying. This was also discussed in chapter 4.1.3, but is emphasised here, as the role of Al (hydr)oxides in retaining P by the soil-sediment mixtures was surprisingly small in the presence of Fe (hydr)oxides. Freshly settled Al is reported to adsorb P from the Fe-associated pool (Rydin and Welch, 1998; Lewandowski et al., 2003), as P is preferably adsorbed by Al in competition between Fe and Al (Ulrich and Pöthig, 2000). However, the cited studies are based on Al chemical additions to lakes or precipitation experiments in a laboratory, which cannot be directly applied to the experiments in this work.

Maximum sorption of anions by metal oxides occurs at pH values near the acidity constant ($pK_a$) of metal cations (Hingston et al., 1967). Because $Fe^{3+}$ ($pK_a$=2.2) is a stronger acid than $Al^{3+}$ ($pK_a$=5.0), Fe (hydr)oxides are superior to Al (hydr)oxides as P sorption components at low pH (Yaghi and Hartikainen, 2013). After all, a large drop in pH was not observed in the mixtures due to sediment addition, which would explain the primary sorption of P on Fe. The pH values were at lowest 6.2–6.7 (from soil initial pH 6.8–7.0) at the highest sediment addition rates (50%). This emphasises an important need for future research to explore which circumstantial aspects in the sediments of natural waters actually affect the competition of P sorption between Al and Fe (hydr)oxides.

a) Ojainen




b) Rehtijärvi

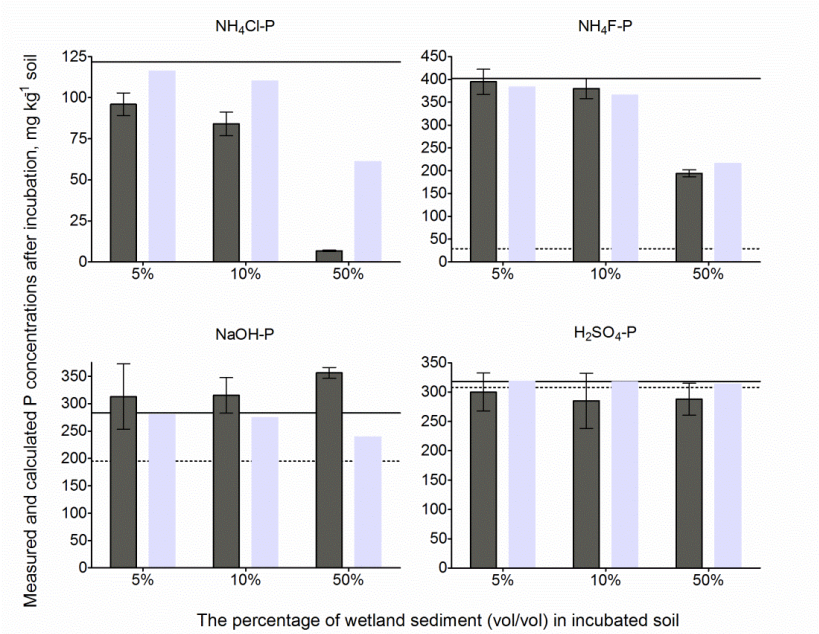



Figure 8. Measured (black bars) and calculated (on the percentage basis of mixtures, grey bars) Chang and Jackson P fractions ($NH_4Cl$-P, $NH_4F$-P, NaOH-P, $H_2SO_4$-P) in the mixtures of a) Ojainen (silty clay, agronomic P test value 24 mg $P_{Ac}$ $l^{-1}$) and b) Rehtijärvi (sandy loam, 210 mg $P_{Ac}$ $l^{-1}$) soils and Liedonperä sediment (soil/sediment, v/v%). A horizontal line shows the P fraction of soil and a dashed line the sediment. Error bars are for 95% significance.

## 4.4 Utilisation of sediment – is it a P source or sink when mixed with field soil?

In the previous sections, a conclusion was made that sediment is nearly depleted in Al-bound P, rich in clay and metal oxide material, and if applied to a field it increases a soil's stock of Al and Fe (hydr)oxides with a low degree of P saturation. Practically, two experiments were performed to investigate what effects returning sediment matter to fields would have on the properties of field soils: first, sediment P availability for ryegrass was tested in a pot experiment (Paper II), and second, a simulated rainfall study was conducted to explore whether sediment additions affect P losses by runoff (Paper III).

### 4.4.1 Sediment P availability for ryegrass

Plant availability of sediment P was tested in a 70-day pot experiment in a greenhouse with Italian ryegrass (*Lolium multiflorum* L.) grown in the Ojainen and Liedonperä soil/sediment mixtures. The sediments were obtained from CWs of the corresponding sites.

NaOH-extractable P in the growth medium, here representing both the Al- and Fe-bound P fractions, showed rather high amounts of potential P availability for ryegrass, especially for the Ojainen soil-sediment mixtures, in which relatively large proportions of all sediment rates were of sediment origin (Table 8). However, the two-point sorption-desorption test suggested that soluble P would be immobilised as a result of sediment application already at the lowest sediment rate (12.5% of dry weight), associated with an $EPC_0$' decrease by 60% on average, as compared with un-amended field soil (see Fig. 7).

Table 8. NaOH-extractable P concentration of Ojainen and Liedonperä soil-sediment mixtures with 0%, 12.5%, 25%, 50% and 100% (by dry weight) sediments. Results are given as means (n=3) ± standard error of mean (SEM).

| Sediment addition rate (%) to soil | NaOH-P (mg $kg^{-1}$) |
|---|---|
| Ojainen | |
| 0 (control) | 258±20 a |
| 12.5% | 320±90 ab |
| 25% | 369±15 bc |
| 50% | 419±6 c |
| sediment | 508±8 d |
| | |
| Liedonperä | |
| 0 (control) | 147±6 a |
| 12.5% | 158±8 ab |
| 25% | 154±3 a |
| 50% | 156±1 ab |
| sediment | 189±8 b |

Values followed by different letters differ significantly ($p$<0.05, Tukey's test). The two sites were tested separately.

In the pot experiment, ryegrass yield was largely unaffected by CW sediment application (Paper II), but P uptake systematically decreased when the rate of sediment application to the soil increased (Fig. 9). When 12.5% of the sediment was added, plant P

uptake as the sum of the three cuts decreased in P-unfertilised pots by 11–28% and in P-fertilised pots (45 mg P pot$^{-1}$) by 13% compared with P uptake of ryegrass grown in un-amended field soil. Sediment material with high amounts of P depleted oxide surfaces thus decreased the plant uptake of P even when P fertiliser was applied in this experiment. As a conclusion, dredged CW sediment may well impair crop P supply if applied to agricultural fields in large quantities.

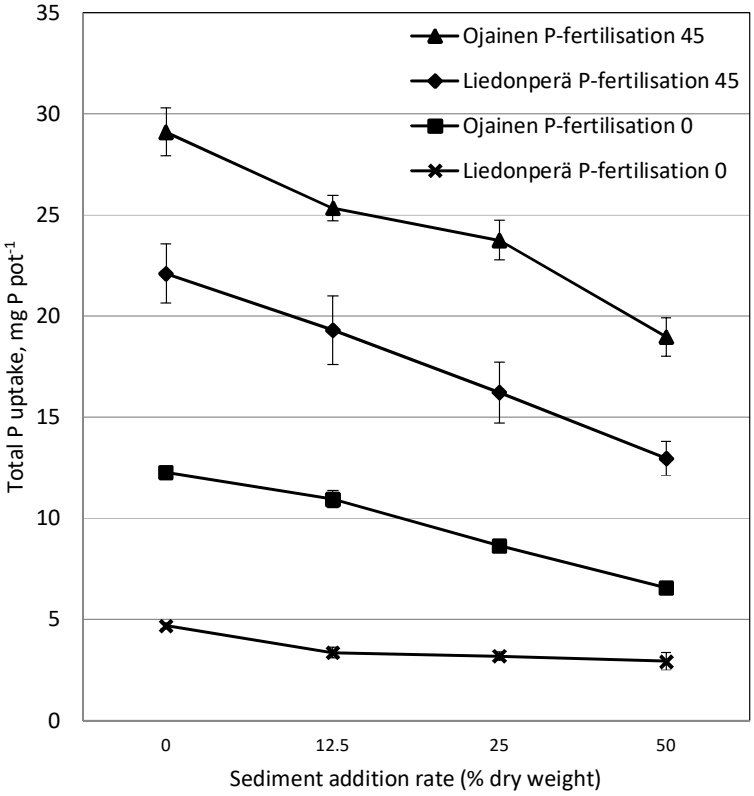



Figure 9. Total P uptake (mg pot$^{-1}$) by ryegrass as a sum of three cuts at 30, 50 and 70 days after sowing from plants grown in Ojainen and Liedonperä soil-sediment mixtures with 0%, 12.5%, 25% and 50% (m-% dry weight) sediment and with P fertilisation of 0 and 45 mg pot$^{-1}$. Results are given as means ± 2 standard deviations (n=3).

### 4.4.2 Use of sediment for P mitigation in critical source areas

As the sediment turned out to act as a P-deprived growth medium in the pot experiment, an opposite viewpoint was considered. A study was planned where sediment was harnessed to mitigate runoff P from soils with high soluble P content (Paper III). The potential of using sediment to decrease phosphorus leaching was tested by a rainfall simulator.

In the rainfall simulation, addition of sediment to soil significantly decreased the dissolved reactive P (DRP) concentration ($p$ value varied between 0.000–0.022) in percolating water at 2–10% sediment application rates (Fig. 10). The decrease was considerable especially for the Rehtijärvi soil with excessive soil test P (210 mg $P_{Ac}$ $l^{-1}$). A sediment addition rate of 5% appeared to decrease the PP concentration ($p$=0.208, not significant, for Ojainen and $p$<0.001 for Rehtijärvi) in percolating water during the early phase of the rainfall simulation event (data shown in Fig. 3 in Paper III). Upon prolonged rainfall, the decreasing effect of sediment on DRP and PP concentrations declined somewhat within each sediment addition rate. Results suggested that sediment application has a short-term and long-term influence on decrease in soil P mobility.

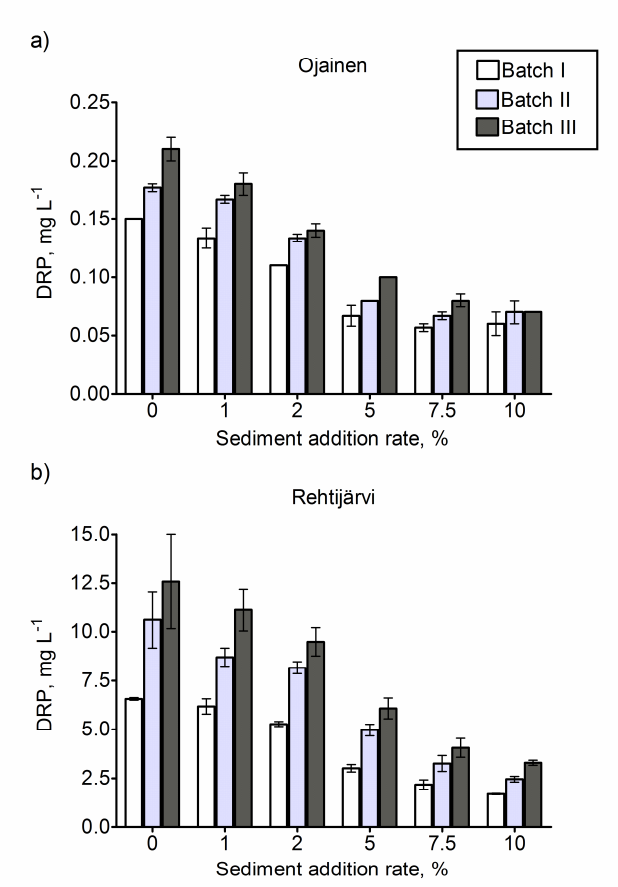



Figure 10. Dissolved reactive P (DRP) in three 100-ml batches (I, II, and III) of percolating water from a simulated rainfall event on (a) Ojainen and (b) Rehtijärvi soil–sediment mixtures with 0, 1, 2, 5, 7.5, and 10% (v/v) sediment. Results are given as means ± SEM.

The mechanism behind this first declining mobilisation of P from sediment addition (short-term) is likely partly related to an increase in salt concentration and thus a rise in

ionic strength, which is known to promote P sorption (Barrow and Shaw, 1979; Yli-Halla and Hartikainen, 1996) and particle aggregation (Haynes and Naidu, 1998). Sediment addition had a slight but increasing influence on electrical conductivity (EC values shown in paper III's supplemental material) in percolating water, which is indicative of the presence of dissolved salts from the applied sediment. As water-soluble salts were leaching out, the effect of sediment addition diminished on prolonged rainfall.

Salts in the sediment most likely originated from the processes occurring in the reduced wetland sediment and reoxidation of the dredged sediment after drying. As mentioned in section 4.1.5, a high S concentration in the CW sediment suggested the presence of Fe sulfides. Oxidation of FeS and $FeS_2$ produces $SO_4^{2-}$ -ions and acidity ($H^+$) to the soil solution and further to the percolating water. Leaching of acidity was also seen as the pH of percolating water increased with prolonged rainfall.

The longer-term effect on P sorption of sediment addition to soil is linked to high clay and Al and Fe (hydr)oxide concentrations in the sediment, but more importantly to the fresh oxide surfaces formed after dredging and oxidation and their low $DPS_\Sigma$, as discussed earlier (and Papers I, II, III).

As a conclusion, dredged sediment from CWs established on clay soils could be used to control P losses from agricultural areas. Due to the low P saturation, this type of use might be beneficial in high-P soils for immobilising easily soluble P from nonpoint sources (Zhang et al., 2002). A practical rate of sediment addition could be $\leq 5\%$ (by fresh volume) to the surface soil layer. With a depth of 20 cm ploughing, this roughly equates to max. 100 $m^3$ of wet sediment to a hectare (or 1 $m^3$ to an are), and of course to lower rates if the depth of mixing is less than 20 cm. These addition rates had a profound decreasing effect on DRP concentrations in percolating water in the simulated rainfall tests.

# 5 Conclusions

- Clay contents of CW sediments were higher than in catchment soils, likely because of selective erosion, transport and settling of fine-sized soil material. CW sediments were believed to originate in the topsoil of cultivated land.

- Despite substantial clay accumulation in the CWs, the fresh sediments contained only slightly higher concentrations of Al and Fe (hydr)oxides than the soils in the field. This may indicate that fine clay particles and colloids (<0.2 μm) were not retained in the CWs.

- Nearly equal concentrations of total P were measured in the soils and sediments, but differences were found in the quantities of Al- and Fe-associated P. In general, the sediment content of Al-P was significantly lower and Fe-P significantly higher than in the soils. Large reserves of redox-sensitive Fe-P were found in the sediments, which might result in mobilisation of P into the water phase during severe anoxia.

- Reduced conditions, conducive to dissolution of Fe (hydr)oxides and accumulation of S in sediments suggested the presence of Fe sulphides. Re-oxidation and drying of the sediments markedly increased the P sorption capacity of eroded soil material, by formation of new, P-depleted oxide surfaces of accumulated Al and Fe compounds.

- Dredged (re-oxidised) sediments showed a high affinity for P in sorption-desorption tests. The more sediment mixed into the soil, the more plant uptake of P for ryegrass decreased in the pot experiment. In the simulated rainfall test the DRP concentration in percolating water lowered with an increasing sediment addition rate into the soil.

- Returning dredged sediment material back to fields surrounding CWs established on fine-textured mineral soils is likely to decrease the amount of P readily available for crop uptake.

- Use of sediments dredged from CWs can be expected to immobilise soil P and decrease nonpoint source P when applied to critical source area soils with problematically high P saturation. A practical rate of sediment addition could be ≤ 5% (by fresh volume) mixed into the plough layer.

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